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CONVEYOR BELT METHOD FOR STUDYING SRORT-LIVED ACTIVITIES: Ag^{108}, Ag^{110} AND In^{116}

By M. C. Joshi and B. V. Thosar

(Tata Institute of Fundamental Research, Bombay 1)

Received March 13, 1956

(Communicated by Prof. B. Peters, F.A.SC.)

Introduction

It is difficult to study in detail the radiations in the decay of short-lived isotopes with half-lives ranging from a second to several minutes. It is necessary to have a high initial source strength in order to allow for the rapid decay in the interval after production and before measurements of its radiations can commence. Some mechanical device has to be used for quickly transferring the source after irradiation to the place of observation. Laborious corrections have also to be made to allow for the decay of the source during measurements. These difficulties have been partly overcome by the use of elaborate electronic devices which permit measurements in a brief period of observation.

It is, however, possible to use a mechanical device in which at one point in a continuously moving sample, spread on an endless conveyor belt, radioactivity is induced, say by (n, γ) reaction, and at another point it is detected and measured. It can be shown that in this case for a given geometrical arrangement and a given speed of the moving belt, a steady equilibrium counting rate is obtained. Usual techniques for measurement of beta and gamma radiations can be employed and apart from the question of source strength, difficulties arising from the rapid decay of a short-lived isotope are eliminated.

In some experiments based on this principle (Nahmias and Walen,[1] and Holmes[2]) the sample was spread on the rim of a rapidly rotating circular hoop, the neutron source and the detector being at opposite ends of a diameter. At the detector, the background counting rate due to the neutron source was high, often higher than that due to the induced activity. The technique of a moving conveyor belt described in this paper makes it possible to choose a distance between the neutron source and the detector such that adequate lead shielding can be installed to reduce the background counting rate to a negligible value. Feeble induced activities can therefore be studied.

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This method also affords greater mechanical flexibility as regards the disposition of the source inducing activity and the detector.

Some results with short-lived isotopes of silver and indium obtained by using this technique are described. Our equipment as now set up is suitable for measuring activities with half-lives ranging from a second to several minutes.

THEORY OF THE METHOD

Consider an arrangement as shown in Fig. 1, in which a conveyor belt of total length L passes near the neutron source R and the counter C. Let the portion of belt within the neutron flux at any instant be of length l_1 and let the portion 'seen' by the counter be l_3, each of these being small compared to L. The length of belt from R to C is l_2.

$\left(\text{In the present arrangement } l_2 \text{ is about } \frac{L}{2}\right)$.

The probability that an activated atom emerges from the region of neutron flux is

$$P = \int_0^{l_1} F \cdot \sigma \cdot \frac{dl}{V} \cdot e^{-\frac{\lambda l}{L} \cdot \tau}$$

where $V = \frac{L}{\tau}$, τ being the period of revolution of the belt.

$$\therefore P = \tau \frac{F\sigma}{L} \int_0^{l_1} e^{-\frac{\lambda l}{L} \cdot \tau} dl$$

$$\therefore P = \frac{F \cdot \sigma}{\lambda} \left(1 - e^{-\frac{\lambda l_1}{L} \cdot \tau}\right). \qquad (1)$$

Here, F is the neutron flux, σ is the capture cross-section for neutrons and λ the decay constant of the induced activity.

The probability that an activated atom leaving the region of neutron flux decays in front of the counter is

$$q = e^{-\lambda \frac{l_2}{L} \cdot \tau} - e^{-\lambda (l_2 + l_3) \frac{\tau}{L}}$$

$$\therefore \quad q = e^{-\frac{\lambda l_2 \cdot \tau}{L}} \cdot \left(1 - e^{-\frac{\lambda l_3}{L} \cdot \tau}\right).$$

The probability that this happens during the second revolution is $q \cdot e^{-\lambda \tau}$.

Hence the total probability that an activated atom decays in front of the counter is

$$Q = e^{-\frac{\lambda l_2 \tau}{L}} \cdot \left(1 - e^{-\frac{\lambda l_3}{L} \cdot \tau}\right)\left(1 + e^{-\lambda\tau} + e^{-2\lambda\tau} + \ldots\ldots\right)$$

$$\therefore \quad Q = e^{-\frac{\lambda\tau}{L} \cdot l_2}\left(1 - e^{-\frac{\lambda\tau}{L} \cdot l_3}\right)\frac{1}{1 - e^{-\lambda\tau}} \cdot \qquad (2)$$

If N_0 is the number of inactive atoms of the sample per unit length of the belt then the number of disintegrations per second counted by the detector is

$$C = K.N_0 \cdot \frac{L}{\tau} \cdot P \cdot Q$$

where K is a constant depending on counter geometry and efficiency.

$$\therefore \quad C = K.N_0 \frac{LF.\sigma}{\tau.\lambda}\left(1 - e^{-\lambda\tau\frac{l_1}{L}}\right)\frac{e^{-\lambda\tau\frac{l_2}{L}}}{1 - e^{-\lambda\tau}}\left(1 - e^{-\lambda\frac{\tau}{L}l_3}\right) \qquad (3)$$

If $\lambda\tau \cdot \frac{l_1}{L} << 1$ and $\lambda T \cdot \frac{l_3}{L} << 1$

$$C = KN_0 F \cdot \sigma \cdot \frac{l_1 l_3}{L} \cdot \lambda\tau \frac{e^{-\lambda\tau \cdot \frac{l_2}{L}}}{1 - e^{-\lambda\tau}} \cdot$$

Putting $x = \frac{\lambda\tau}{2}$ and $l_2 = \frac{L}{2}$,

$$C = \left(KN_0 F\sigma \frac{l_1 l_3}{L}\right)\frac{2x \cdot e^{-x}}{1 - e^{-2x}}$$

$$\therefore \quad C = C_0 \frac{x}{\sinh x} \cdot \qquad (4)$$

C_0 is a constant depending on counter geometry and efficiency, thickness and density of the sample, neutron flux and capture cross-section and is independent of decay constant and period of revolution of the belt, provided $\lambda\tau \frac{l_1}{L}$ and $\lambda\tau \frac{l_3}{L}$ are small compared to unity.

When a single activity of decay constant λ is present the variation of $\frac{x}{\sinh x}$ with the period of revolution τ is that shown in curve *a* of Fig. 2. At high speeds of the belt $\frac{x}{\sinh x}$ approaches unity and the saturation counting rate C_0 is reached. One can see that when $\frac{\tau}{T} = 0{\cdot}1$, where T is the half-life, $\frac{x}{\sinh x}$ is very nearly equal to unity. When $\frac{\tau}{T} = 1$ this

differs very little from unity. Therefore, to obtain saturation counting rate C_0, the period of revolution τ must not be more than T. This falls to half the saturation value $\frac{C_0}{2}$ at $\tau = 6{\cdot}3\,T$, where T is half-life of the activity. Any deviation from this would indicate the presence of more than one short-lived activity. When one activity is present it is possible to calculate the half-life from observations of the counting rate at different periods of revolution of the belt.

When two short-lived activities are simultaneously present, at high speeds of the belt (when $\tau < T_1$ or T_2), the saturation counting rate due to each of them individually can be calculated from the observed saturation rate if the relative isotope abundance and capture cross-sections are known. As the period of the belt is increased the contribution to the counting rate from the shorter-lived activity decreases more rapidly than that from the longer-lived one. It is possible in favourable cases to choose a period of the belt at which the contribution from the shorter-lived activity is negligible and the longer-lived activity can be investigated without interference from the former. It is also possible to calculate the half-life of one of the activities if that of the other is known, making use of known relative isotope abundance and capture cross-sections.

EXPERIMENTAL ARRANGEMENT AND OBSERVATIONS

Fig. 1 shows the experimental arrangement used for the present investigations. The endless belt B, 20 feet in length, runs over two pulleys A, each 1 foot in diameter. One of the pulleys is coupled to a motor specially designed for this purpose and capable of giving continuously variable speeds up to a maximum of 1400 rev. per minute. The belt passes through a cavity in a paraffin block P which also contains at R, just below the belt, a Radium-Beryllium source of neutrons of strength 500 m.c. L is a heavy lead shield surrounding the paraffin block. The pulleys A were arranged in two adjacent rooms with the wall W separating them for better shielding. At C an end-window Geiger counter was used for beta-ray counting and a scintillation counter for gamma-ray measurements. The length of belt from R to C was half its total length. The counter C, which was adequately shielded by surrounding lead, was so arranged that aluminium absorbers could be interposed between its window and the sample on the belt.

With the Ra-Be source in position the background counting rate was determined for no sample on the belt, both when the belt was at rest and in motion. The background rate in both the cases was found to be 25 counts per minute, only a few counts more than the natural background.

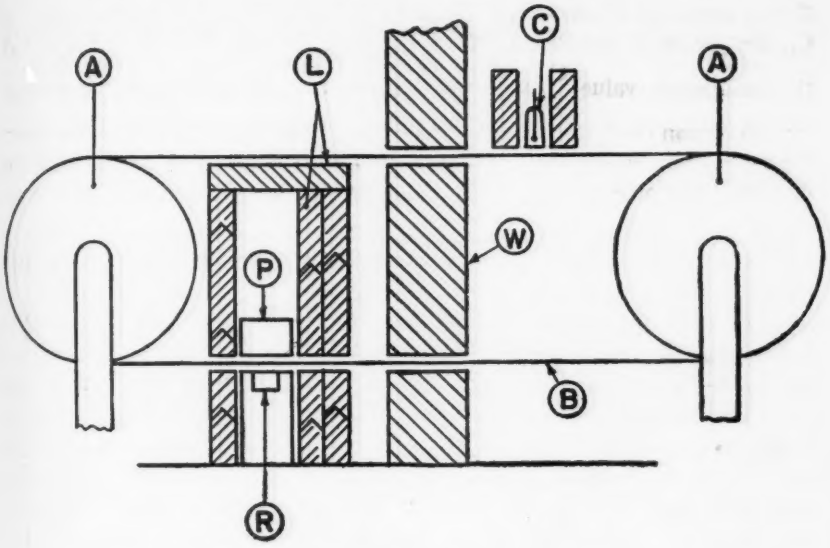

FIG. 1. Experimental Arrangement.

Silver strips of 240 mgm./cm.^{2} thickness were fixed along the whole length of the belt and the counting rate was determined for various values of the period of revolution in the range 5 sec. to 300 sec. The experimental points are shown in Fig. 2, on the curve C.

Two activities are known to be induced in silver by slow neutron capture,[3, 4] 22·5 sec. Ag^{110} and 2·3 min. Ag^{108}. The relative abundance of the stable isotopes Ag^{109} and Ag^{107} as well as their capture cross-sections being known, the relative proportions of the two activities in the total activity induced can be calculated. The total maximum counting rate C_0 is made up of maximum counting rate (C_{01} due to 22 sec. Ag^{110} and C_{02} due to 2·3 min. Ag^{108}. C_{01} and C_{02} were calculated from the observed maximum counting rate of about 700 c./min. Making use of the equation (3), and using the known values of the decay constants of the two activities, curves *a* and *b* in Fig. 2 were constructed, showing the variation of counting rate with period of revolution for the two individual activities. Curve C is the sum of these two curves *a* and *b*, and indicates the variation of counting rate with period of revolution to be expected when both activities are simultaneously present. The experimental points obtained for the counting rate at different speeds are seen to lie close to the theoretical curve C. It may also be seen from curve C in Fig. 2 that while at the shorter period of revolution, $\tau = 5$ sec., the observed effect depends on both the activities, at lower speeds, with τ

greater than 300 sec. the effect of the shorter-lived Ag^{110} is substantially reduced and the activity of Ag^{108}, half-life 2·3 min., becomes preponderant. By adjusting the speed of the belt one can, in favourable cases, filter out the effect of the shorter-lived activity whenever two short-lived activities are present. The other activity can, therefore, be investigated in a convenient manner.

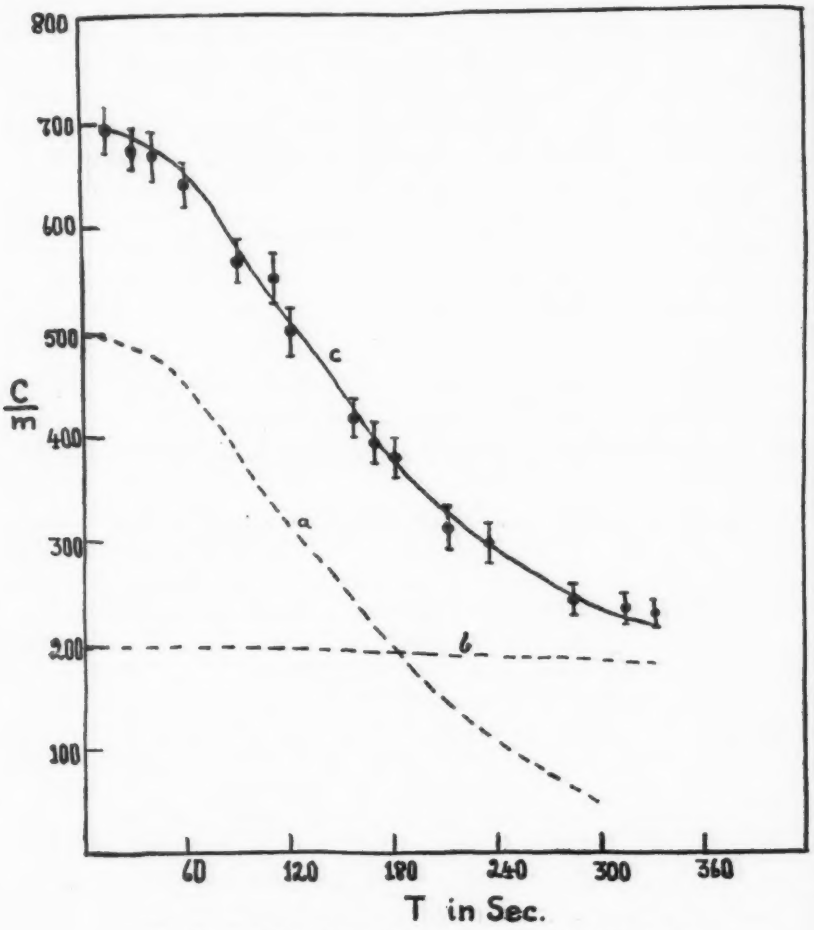

FIG. 2. Variation of Counting Rate with Period; Ag^{108}, Ag^{110}.

By using accurately calibrated aluminium absorbers, absorption curves for beta-rays were obtained for two periods of revolution of the belt, for

$\tau = 5$ sec. when beta-rays due to both Ag^{108} and Ag^{110} were present and for $\tau = 300$ sec., when beta-rays due to Ag^{108} alone were preponderant. These absorption measurements were used to get the maximum energies of the beta-ray groups as shown in Fig. 3.

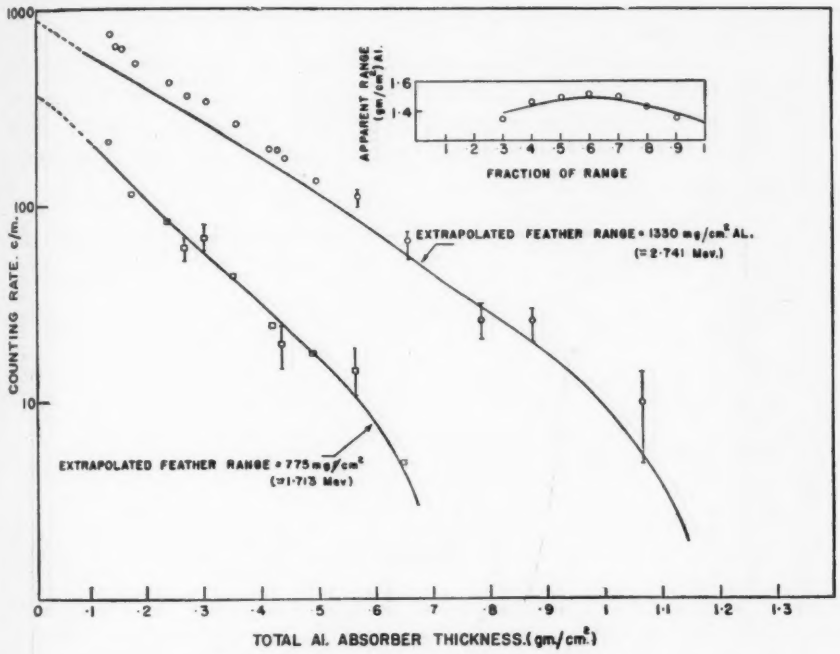
1000
100
10
COUNTING RATE. c/m.
APPARENT RANGE (gm/cm²) Al.
1·6
1·4
1 2 3 4 5 6 7 8 9 1
FRACTION OF RANGE
EXTRAPOLATED FEATHER RANGE = 1330 mg/cm² AL.
(= 2·741 Mev.)
EXTRAPOLATED FEATHER RANGE = 775 mg/cm²
(= 1·713 Mev.)
0 ·1 ·2 ·3 ·4 5 6 7 ·8 ·9 1 1·1 1·2 1·3
TOTAL Al. ABSORBER THICKNESS. (gm/cm²)

FIG. 3. Absorption of Beta-Rays; Ag^{108}, Ag^{110}.

A scintillation spectrometer consisting of a NaI (Tl) crystal, E.M.I. 6262 photo-multiplier tube and a single channel pulse-height analyser, was used to investigate the gamma-ray spectra, using the same two speeds of the belt.

RESULTS

The absorption curve (Fig. 3) obtained at the faster speed of the belt indicates two beta-ray groups with maximum energies at $2{\cdot}7 \pm {\cdot}1$ MeV. and $1{\cdot}7 \pm {\cdot}1$ MeV. In the absorption curve at the slower speed the beta-ray group of maximum energy 1·7 MeV. is observed but not the other one at 2·7 MeV. showing that the latter is due to the decay of 22 sec. Ag^{110} and the former due to 2·3 min. Ag^{108}. This is in agreement with the results of scintillation spectrometer studies of Ag^{110} by M. Goodrich[5] and of Ag^{108}

by Goodrich *et al.*[6] There is also an indication of another beta-ray group of maximum energy 0·75 MeV. due to Ag^{103}. To explain this one has to assume that in addition to 0·6 MeV. gamma-ray another gamma-ray of 0·4 MeV. is emitted in cascade in the beta-decay of Ag^{108}. This is not inconsistent with the gamma-rays observed with the scintillation spectrometer.

Fig. 4 shows the gamma-ray peaks at 0·4 MeV., 0·5 MeV., 0·6 MeV. and 0·9 MeV. obtained with the scintillation spectrometer, for a speed of the belt so high that both activities, Ag^{108} and Ag^{110} were present. At a lower speed when Ag^{108} alone is effective,[7] the peak at 0·9 MeV. disappears, showing that it is due to Ag^{110}.

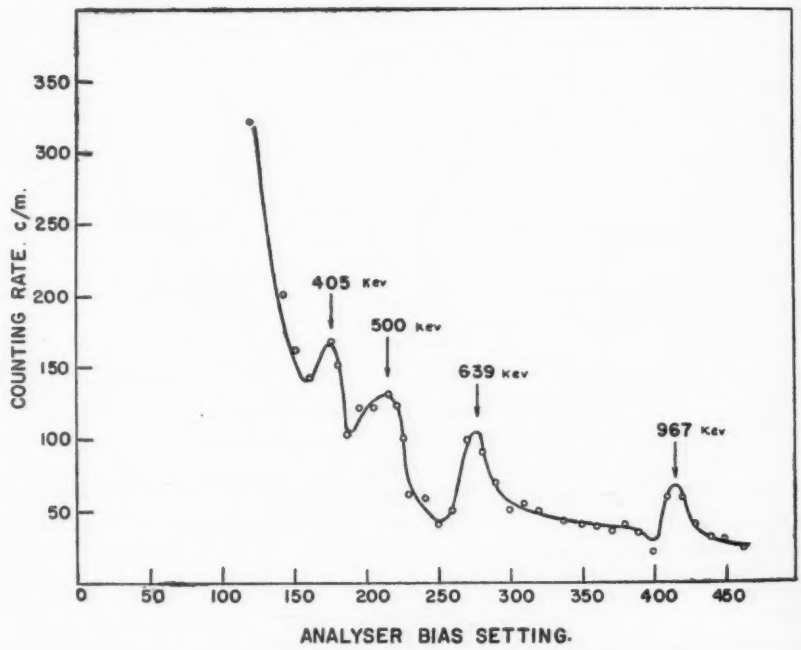

FIG. 4. Gamma-Ray Spectrum by Scintillation Spectrometer.

Another experiment was carried out in which Indium foil was placed on the belt. The counting rate was measured at different times from the start of the experiment, the period of the belt remaining constant at 3 sec. per revolution. $Indium^{116}$ has two activities of half-life 13 sec. and 55 min. respectively. Saturation counting rate due to 13 sec. activity is reached

within about one minute after start while that due to 55 min. activity increases with time and reaches saturation after 3 hours (Fig. 5). The observed ratio of the saturation counting rates for the two activities agrees with the ratio of the known capture cross-sections for the production of the two activities.

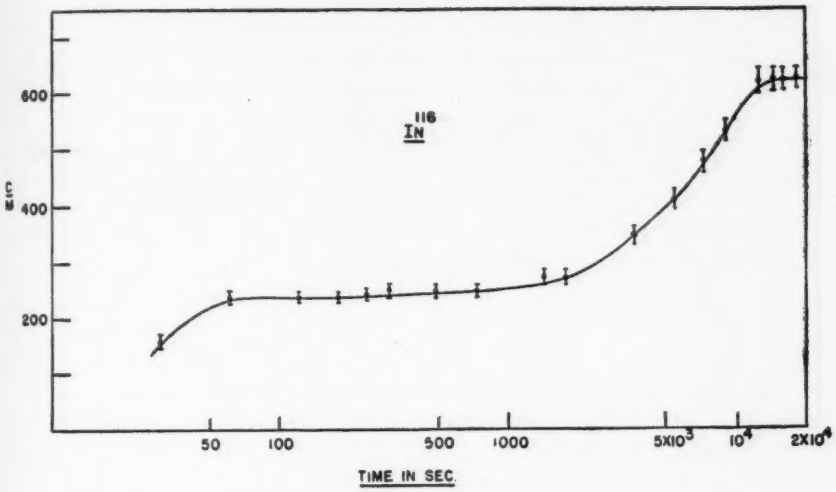

FIG. 5

SUMMARY

A technique for studying short-lived radio-activities is described. It is suitable for half-lives in the range from a second to several minutes. The activity is induced at one point in the sample spread over a moving, endless conveyor belt and is studied at another point. The equilibrium counting rate then depends on the speed of the belt. The activity of 22 sec. Ag^{110} and that of 2·3 min. Ag^{108} have been studied. The maximum energies of beta-ray groups were determined from absorption curves. Gamma-ray energies were obtained with a scintillation spectrometer. It is shown that in favourable cases, when two short-lived activities are present, the shorter-lived one can be filtered out by adjusting the speed of the belt.

The authors believe that the technique can easily be adapted to an experiment where irradiation is obtained by means of a reactor and can be of great value when making detailed investigation of radiations from short-lived isotopes.

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REFERENCES

1. Nahmias, M. E. and Walen, R. J. — *J. Phys. Rad.*, 1937, **8**, 153.
2. Holmes, J. E. R. .. *Proc. Phys. Soc.*, 1949, **62 A**, 293.
3. Pool, M. L. .. *Phys. Rev.*, 1938, **53**, 116.
4. Perlman, M. L. and Freidlander, G. — *Ibid.*, 1948, **74**, 442.
5. Goodrich, M. .. *Ibid.*, 1951, **82**, 759.
6. ———, and Cambell, E. C. — *Ibid.*, 1952, **85**, 742.
7. Perlman, M. L., *et al.* .. *Ibid.*, 1953, **92**, 1236.

STUDIES ON HEXACHLOROCERIC ACID

III. Reaction between Hydrated Ceric Oxide and Hydrogen Chloride Gas in the Absence of Solvents

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Received February 25, 1956

It has been observed by earlier workers that when ceric hydroxide is added to concentrated hydrochloric acid, a dark brown solution is obtained. The colour of the solution is lost slowly on standing or rapidly by warming, with evolution of chlorine. The development of colour is assumed to be due to the formation of ceric chloride or hexachloroceric acid. Koppel[1] thought that water was responsible for the instantaneous decomposition of the product formed in the above reaction. He and subsequent workers therefore attempted to prepare the salt from non-aqueous medium.

The reaction between hydrated ceric oxide and hydrogen chloride gas has been investigated in detail. In these experiments, dry hydrogen chloride gas is allowed to react with hydrated ceric oxide without a medium for suspending the oxide. These studies have proved that the chloro-compound of ceric cerium can be obtained in a solid form. The reaction studied now can be represented as:

$$CeO_2 \cdot nH_2O + 6\ HCl \rightarrow H_2CeCl_6 \text{ or } CeCl_4 \cdot 2\ HCl + (n + 2)\ H_2O.$$

Anhydrous ceric oxide does not react with hydrogen chloride, due to the passivity of ceria which is prepared by the ignition of the hydroxide at 800° C. The reaction, however, does not appear to be as simple as represented in the above equation. A serious handicap in understanding the mechanism of this reaction is the lack of knowledge regarding the structure of hydrated ceric oxide. Whether an oxonium type of intermediate compound of hydrogen chloride with all or any of the oxygen, is formed cannot be predicted with the knowledge gained by the present studies.

These studies have, however, shown that although immediate decomposition of ceric compound formed will take place by the presence of free water, yet combined water with ceric oxide is helpful in the production of hydrochloroceric acid. Actually, the maximum reaction is found to take place, when the hydrate corresponds to $CeO_2 \cdot 4\ H_2O$. The formation of the brownish red colour is also much quicker when the percentage of water in the oxide is higher. A possible explanation is afforded by assuming that

hydrogen chloride would react with water to give the hydroxonium and chloride ions which will then react with CeO_2.

When the hydrated ceric oxide reacts with hydrogen chloride, the water that is set free will catalytically decompose the ceric chloride formed. In the reactions where dioxane, methyl alcohol, etc., are used as reaction media the free water is taken up by the solvent and the deleterious effect of water is largely overcome. The greater stability of the product at lower temperature may be due, besides the temperature effect, to the two phase system of the compound and water.

Although it has not been possible to isolate the hexachloroceric acid in a state of purity, the studies made on the thermal decomposition of the acid indicate that the compound formed is not ceric chloride but has the formula H_2CeCl_6. From the analogy of the composition of the crystals isolated from dioxan and from the fact that water is given off during decomposition, it appears reasonable to assume that the compound contains water of crystallisation.

EXPERIMENTAL

Materials used

Hydrated ceric oxide and hydrogen chloride were prepared as described earlier.[1] Other reagents used were of A.R. quality.

Effect of temperature on the reaction of hydrated ceric oxide and hydrogen chloride gas

Dry hydrogen chloride gas was passed over a weighed quantity of hydrated ceric oxide ($CeO_2 \cdot 2H_2O$) placed in a U-tube at constant temperature. The outgoing gases were bubbled through a wash bottle containing potassium iodide solution. The chlorine that was evolved during the reaction, due to the decomposition of the ceric chloride, reacted with the potassium iodide solution and liberated iodine which was estimated by standard sodium thiosulphate solution. After carrying out the reaction for 30 minutes at a constant temperature and estimating the amount of decomposition during this period, a fresh quantity of potassium iodide was placed in the wash bottle and the U-tube was heated to 40° C. The chlorine produced was swept off by a current of nitrogen into potassium iodide solution and the iodine liberated estimated. The total per cent. conversion of ceric oxide and per cent. decomposition during the reaction were then calculated.

The U-tube was first cooled in liquid air. When the solid hydrogen chloride that had deposited in the U-tube had completely covered the ceric oxide, the tube was tapped gently to mix the contents, the liquid air-bath

was removed and the U-tube placed in a mixture of solid carbon dioxide and alcohol. The deposited hydrogen chloride volatilised without effecting any change to the ceric oxide. There was no colour change in the potassium iodide solution. The U-tube was then maintained at — 20° C. and hydrogen chloride gas passed for 30 minutes. The ceric oxide turned orange brown in colour. There was slight liberation of iodine in the potassium iodide solution. The amount of decomposition during the reaction period and the percentage of conversion of ceric oxide were estimated. The experiment was repeated with known weights of hydrated ceric oxide at — 10° C., 0° C., 10° C and 20° C. The results are presented in Table I.

TABLE I

Effect of temperature on the reaction of hydrogen chloride gas with hydrated ceric oxide, $CeO_2.2H_2O$

Reaction period: 30 Minutes

Bath Temperature	Per cent. decomposition during reaction	Per cent. total reaction between ceric oxide and HCl gas
Liquid air	Nil	Nil
Solid carbon dioxide..	Nil	Nil
—20° C.	37·0	9·1
—10° C.	38·5	14·6
0° C.	40·5	25·2
10° C.	46·9	35·7
20° C.	57·2	50·1

These results indicate that at higher temperatures, the extent of reaction is greater, but the per cent. decomposition is also higher.

Effect of dilution or hydrogen chloride gas with nitrogen

As the reaction between hydrated ceric oxide and hydrogen chloride gas is highly exothermic and as heat decomposes the reaction product, the effect of diluting hydrogen chloride with nitrogen was next investigated. Nitrogen was bubbled through hydrochloric acid (12 N) and the mixture of hydrogen chloride vapour and nitrogen dried over P_2O_5 was passed over

a known weight of hydrated ceric oxide. The temperature was maintained at − 15° C. and the gaseous mixture was passed for 30 minutes. The experiment was repeated by bubbling nitrogen at the above rate through hydrochloric acid of different strengths to reduce the amount of HCl in the gaseous mixture. The amount of decomposition during the reaction and the percentage conversion of ceric oxide were determined as described previously. It was found that reasonably high yields of the product were obtained when the gaseous mixture got by bubbling nitrogen through 6 N hydrochloric acid is used (per cent. conversion = 41·6; per cent. decomposition = 6·1).

Effect of increasing the reaction surface of ceric oxide

Since the reaction is between gaseous hydrogen chloride and solid ceric oxide, it can be expected to increase by increasing the effective area of ceric oxide. The U-tube was loosely packed with dry glass wool and 0·5 g. of the oxide spread over it and nitrogen bubbled through 6 N hydrochloric acid, passed for 30 minutes at − 15° C. It was found that nearly 70% of the ceric oxide was converted into chloride, 22·5% of which decomposed during the reaction.

Influence of the degree of hydration of ceric oxide on the reaction

In the previous experiments, the ceric oxide employed had 17·5% water corresponding to the formula $CeO_2 \cdot 2H_2O$. The influence of the degree of hydration of ceric oxide was next investigated. Ceria obtained by the ignition of cerous oxalate at 800° C. was employed as the sample containing zero amount of water and a hydrate corresponding to the composition $CeO_2 \cdot \frac{1}{2} H_2O$ was prepared by heating the dihydrate at 120° C. for 6 hours. Another hydrate corresponding to $CeO_2 \cdot H_2O$ was prepared by drying the dihydrate over phosphorous pentoxide for three days. A sample of the dihydrate was kept in a vacuum desiccator over water at 28° C. to get a hydrated oxide corresponding to the formula $CeO_2 \cdot 4\ H_2O$. Freshly precipitated ceric hydroxide was filtered, pressed between folds of filter-paper and was dried over phosphorous pentoxide till a hydrate corresponding to the formula $CeO_2 \cdot 8\ H_2O$ was obtained.

A known weight of each of the oxides was treated as before with hydrogen chloride gas diluted with nitrogen. The oxide was spread on glass wool maintained at − 15° C. The amount of decomposition and total conversion of the oxide were estimated as in the previous experiments. The results are presented in Table II.

The results of these experiments indicate that ignited ceric oxide does not react with hydrogen chloride gas. As the amount of water retained

TABLE II

Influence of the degree of hydration of ceric oxide on its reaction with hydrogen chloride

Nature of oxide used	Per cent. conversion	Per cent. decomposition
Ignited CeO_2	Nil	Nil
$CeO_2 \cdot \frac{1}{2} H_2O$ ..	16·0	7·5
$CeO_2 \cdot H_2O$	37·2	14·8
$CeO_2 \cdot 2 H_2O$	66·8	21·8
$CeO_2 \cdot 4 H_2O$	82·5	24·6
$CeO_2 \cdot 8 H_2O$	86·7	25·6

by the ceric oxide increases, the percentage conversion also increases. When the composition of the oxide corresponds to $CeO_2 \cdot 4 H_2O$, a conversion of 80–85% is obtained while the decomposition is about 25%. It is therefore possible to prepare H_2CeCl_6 with an yield of about 60%.

Stability of the reaction product at various temperatures

In order to find out the maximum temperature to which the reaction product could be heated without considerable decomposition, a study of the effect of temperature on the stability of the reaction product was carried out. The reaction was carried out as before with 1·0 g. of $CeO_2 \cdot 4 H_2O$ at − 15° C. for 30 minutes. The potassium iodide bubbler was then replaced by a fresh one and dry nitrogen was passed for a period of 15 minutes through the U-tube at each of the following temperatures changing the potassium iodide at each change of temperature.

− 40° C., −20° C., −10° C., 0° C., 10° C., and 20° C.

The amount of decomposition was estimated in each case by the thiosulphate method. Table III gives the results.

These results indicate that at very low temperature the product formed by the reaction between hydrated ceric oxide and hydrogen chloride gas is stable but with increase in temperature the stability is very much diminished. At 20° C. nearly 80% decomposes within 15 minutes. It is of interest to note that when the temperature is raised to 40° C., the decomposition would be nearly complete within 5 minutes.

TABLE III

Stability of the reaction product at various temperatures

Temperature (° C.)	Per cent. decomposition in 15 minutes
−40	1·2
−20	6·5
−10	11·2
0	26·8
10	51·8
20	81·8
40	96·0 (5 minutes)

From these experiments it was clear that the optimum conditions for the formation and stability of H_2CeCl_6 were:

(1) to use hydrated ceric oxide corresponding to $CeO_2 \cdot 4H_2O$; (2) to increase the surface of reaction between the ceric oxide and hydrogen chloride gas; (3) to carry out the reaction between − 20 and − 15° C.; (4) to pass dry hydrogen chloride gas diluted with nitrogen.

All attempts to purify the product failed. The compound could not be purified by sublimation under reduced pressure at − 10° C. on account of the non-volatility of the product. When the temperature was raised to 10–20° C., the compound decomposed considerably. Sublimation experiments in an atmosphere of chlorine or hydrogen chloride gas did not prove successful in purifying the compound. Inert solvents like carbon tetrachloride could not be employed to purify the compound on account of its insolubility. Solvents, like dioxane or methyl alcohol in which the substance was soluble, did not in any way help in the purification of the compound, since the substance would not crystallise in methyl alcohol while from dioxane the substance crystallised with dioxane of crystallisation. The crystals isolated from dioxane analysed to the formula, $H_2CeCl_6 \cdot 4\ C_4H_8O_2$.

Summary

A solvent is not necessary for the reaction of hydrogen chloride with hydrated ceric oxide to form hexachloroceric acid. The product of reaction is stable at low temperatures. Under optimum conditions, the percentage of hydrochloroceric acid produced was about 60.

Acknowledgement

The authors are thankful to Prof. K. R. Krishnaswami for his keen interest and helpful suggestions during the course of the work.

Reference

Moosath, S. S. and Rao, M. R. A., *Proc. Ind. Acad. Sci.*, 1956, **43A**, 213.

STUDIES ON HEXACHLOROCERIC ACID

IV. Thermal Decomposition of Hexachloroceric Acid

By S. S. Moosath

(Department of General Chemistry, Indian Institute of Science, Bangalore)

Received February 25, 1956

(Communicated by Dr. M. R. A. Rao, F.A.SC.)

In Part III of this series,[1] optimum conditions for the reaction of hydrogen chloride gas and hydrated ceric oxide have been described. It has been proved by analysis of the product obtained after crystallisation from dioxane that hexachloroceric acid is formed during the above reaction. Details of the characterisation of the reaction product, and the product of decomposition by heat, are presented in this paper. Although it has not been possible to isolate the reaction product in a pure form from the unreacted ceric oxide and the cerous chloride, these studies indicate that the compound formed is not ceric chloride, but has the composition H_2CeCl_6. From the analogy of the composition of the crystals isolated from dioxane, and from the fact that water is given off during the decomposition of the product, it is most likely that the compound contains water of crystallisation.

Experimental

A known weight of hydrated ceric oxide was made to react with hydrogen chloride at $-15°$ C. by the technique described in Part III of the series. Dry nitrogen was passed through the U-tube for 30 minutes to displace all the hydrogen chloride gas in the system. The chlorine evolved (Table I-A) during the reaction was estimated by absorbing in potassium iodide solution as before. The hydrogen chloride liberated along this chlorine, during the decomposition of the compound could not be estimated since excess of hydrogen chloride gas was passed during the preparation of the compound. Hence the amount of hydrogen chloride (Table I–B) liberated during this decomposition is assumed to be twice the active chlorine estimated by the potassium iodide method as supported by the results of columns C and D of the same table. Two gas bubblers containing 1 N sodium hydroxide solution kept at 2–3° C. were then connected in the place of the potassium iodide solution. The U-tube was heated to 25° C. maintaining the current of nitrogen. The chlorine and hydrogen chloride that were liberated got absorbed by the sodium hydroxide solution. After about 30 minutes the U-tube was heated to about 40° C. and kept at that temperature for 10 minutes to ensure complete decomposition. The alkali solutions were mixed

and made up to 250 c.c. and the hypochlorite and total chloride were estimated in aliquots of this solution by standard methods. From these results, the amounts of chlorine and hydrogen chloride produced were calculated (C and D). The residue left in the U-tube was taken up with water, filtered and the filtrate made up to a known volume. Cerium (E) and chloride (F) contents in this solution were estimated to compute the amount of cerous chloride produced during decomposition. The results are presented in Table I.

The results of Table I (E and F) show that the molar ratio of cerium to chloride in the soluble portion of the residue in the U-tube is as 1 : 3. This indicates that the U-tube contains cerous chloride formed during the decomposition. The calculated ratio of active chlorine, hydrogen chloride and cerous chloride in the compound correspond to the formula, H_2CeCl_6. It is also clear that during the decomposition (C and D), about two moles of hydrochloric acid are expelled for every atom of active chlorine. It can, therefore, be concluded that the brownish red compound formed during the above reaction is H_2CeCl_6.

It has already been shown that, when H_2CeCl_6 is crystallised from dioxane solution, the acid contained four molecules of dioxane of crystallisation. It was of interest to find out whether the complex obtained by the action of hydrogen chloride gas on hydrated ceric oxide, had also some water of crystallisation. With this in view, the following procedure was adopted for the determination of water produced during the decomposition of the compound.

The excess hydrogen chloride gas present in the U-tube, after the reaction, was removed as described previously by dry nitrogen. The U-tube was then connected to a weighed absorption tube containing magnesium perchlorate. The perchlorate tube was connected to a second perchlorate tube and finally to potassium iodide absorbers. The U-tube containing the complex was heated to 20° C. maintaining the current of nitrogen for about 30 minutes, when the complex got decomposed. The magnesium perchlorate tube was then weighed to find out the amount of moisture swept off from the U-tube. The perchlorate tube was again connected in the system and nitrogen passed for another 10 minutes, after which the absorption tube was weighed. There was no further increase in weight, thereby indicating that no water was swept off by the nitrogen from the U-tube. The iodine liberated in the potassium iodide solution was employed to estimate the amount of decomposition of the complex while the increase in weight of the first perchlorate gave the corresponding amount of water that was

TABLE I

Reaction products obtained during thermal decomposition of hexachloroceric acid

Cl_2 gas absorbed by the KI sol. mg.-atoms A	Corresponding value for HCl (2A) m. moles B	Cl_2 gas absorbed by the alkali mg.-atoms C	HCl gas absorbed by the alkali m. moles D	Cerium as cerous chloride mg.-atoms E	Chlorine of the cerous chloride mg.-atoms F	Ratio of Ce : Cl : HCl (E) : (A+C) : (B+D)
0·82	1·64	2·40	5·10	3·31	10·2	1 : 0·97 : 2·04
0·87	1·74	2·28	5·04	3·28	10·2	1 : 0·96 : 2·07
0·84	1·68	2·32	5·03	3·26	10·1	1 : 0·97 : 2·05
Average Values:						
0·84	1·69	2·33	5·06	3·29	10·2	1 : 0·97 : 2·05

swept off from the U-tube. A blank experiment indicated that the passage of a mixture of dry chlorine and hydrogen chloride through the perchlorate absorption tube did not show a detectable increase in weight. The following are the values obtained for moisture when samples of ceric hydroxide containing varying amounts of water of hydration were employed.

TABLE II

Composition of hydrated ceric oxide	Total water in the ceric oxide used mg.	Amount of complex decomposed mg. of Ce	Mg. of water taken up by perchlorate
$CeO_2 \cdot \frac{1}{2} H_2O$	50·0	8·2	3·2
$CeO_2 \cdot H_2O$	95·6	30·8	41·8
$CeO_2 \cdot 2 H_2O$	175·2	56·5	49·2
$CeO_2 \cdot 4 H_2O$	296·0	58·5	67·6

The results of Table II indicate that for every part of the cerium, nearly an equal weight of water is eliminated indicating thereby nearly 10 moles of water for every mole of the hexachloroceric acid decomposed. This large proportion of water is probably due to the decomposition of the hexachloroceric acid during the formation of the compound. It can therefore be concluded that the water associated with the hexachloroceric acid cannot be estimated unless the compound is prepared in a state of purity.

The substance formed during the above reaction was further confirmed to be hexachloroceric acid by the analysis of the compound in dioxane solution. Dioxane was added to the U-tube when the brownish red compound dissolved completely, yielding an orange-red solution. The solution was filtered and analysed for cerium, active chlorine and total chloride. It was noticed that the ratio of cerium to active chlorine to total chloride in this solution was as 1 : 1 : 6·2 corresponding to the formula H_2CeCl_6.

The author is thankful to Dr. M. R. A. Rao and Dr. A. R. Vasudeva Murthy for their keen interest in the work.

REFERENCE

Moosath, S. S. and Rao, M. R. A., *Proc. Ind. Acad. Sci.*, 1956, **43A**, 265.

SPECTROPHOTOMETRIC ESTIMATION OF URANIUM (VI) BY MORELLIN

By B. R. Lakshman Rao and C. C. Patel

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(Communicated by Prof. K. R. Krishnaswami, F.A.SC.)

Colorimetric methods for the estimation of uranium have been suggested by several workers. Inorganic reagents like thiocyanate,[1,2] hydrogen peroxide[3] and ferrocyanide[4] as well as organic reagents like thioglycolate,[5] salicyl amide,[6] dibenzoylmethane[7] and morin[8] have been employed and the methods studied in the presence of various cations and anions. It appears, however, that since no specific reagent for uranium has been discovered so far, the proposed methods are only of limited application and many of them lack sensitivity.[4]

During our studies on spectrophotometric estimation of thorium by morellin,[9] we noticed that even very low concentrations of uranium caused an interference. We, therefore, undertook a study of the uranium-morellin complex with a view to developing a method for estimation of uranium.

Morellin is almost insoluble in water, but fairly soluble in alcohol. An alcoholic medium was, therefore, necessary for these studies. The reddish brown-coloured complex of morellin with uranyl ions appeared instantaneously on mixing the respective solutions and no fading could be observed even after keeping for several days. The coloured complex was, however, destroyed by acid or alkali.

Experimental

Reagents and apparatus

Standard uranium solution.—Baker's analysed sample of uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, was dissolved in distilled water and the solution standardised gravimetrically by the ammonia and the tannic acid methods. There was good agreement in the weight of the U_3O_8 obtained by the two methods. This stock solution contained 4·640 g. U_3O_8 per litre and was preserved in an amber-coloured glass stoppered bottle. For spectrophotometric studies, this solution was diluted to the desired concentration of uranium with aqueous alcohol so that the final strength of alcohol was 50%.

Reagent solution.—A stock solution of morellin was prepared by dissolving 0·7353 g. of recrystallised morellin in a litre of absolute alcohol. The solution had $1·352 \times 10^{-6}$ mole/ml. of morellin.

The other reagents employed were of A.R. quality.

Apparatus used.—Spectrophotometric measurements were made with Coleman universal spectrophotometer model 14, with purple filter 14–214 (PC-4) of special glass, intended for the visible region. Cuvettes (14–302) had an optical path of 1·58 cm. The instrument was worked at a constant band width of 35 mμ in the visible region.

All pH measurements were made by the glass electrode method.

Absorption spectra

The spectral characteristics of morellin in aqueous alcohol medium with 50% alcohol as reference liquid showed an absorption maximum at 410 mμ.[9] Uranyl nitrate solution was found to have an absorption maximum in the region 435–440 mμ. With 50% alcohol as reference solution, the absorption spectrum of the mixture of morellin and uranium in the mole ratio of 8 : 1 gave absorption maxima at 430 mμ and at 540 mμ. Employing morellin solution as a reference liquid, absorption curve A (Fig. 1) was obtained for a mixture of 0·6 ml. of $1 \cdot 365 \times 10^{-3}$ M uranyl mitrate solution and 5 ml.

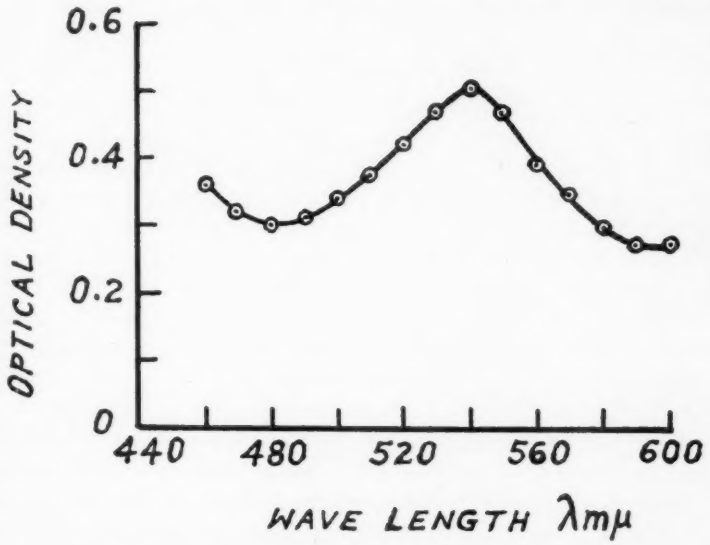


FIG. 1. Absorption Spectrum of Uranyl-Morellin Complex.

of morellin solution of the same concentration made up to 10 ml. by 50% alcohol. The curve shows an absorption maximum at 540 mμ. Since at 540 mμ, the individual absorption by morellin and by uranyl nitrate is

negligible, the maximum at 540 mμ was employed for subsequent spectrophotometric investigations on uranyl-morellin complex.

Effect of light on uranyl-morellin complex in alcohol

Bhattacharyya and Gulvady[10] reported that a photochemical reaction occurs between uranyl ions and alcohol, forming aldehyde and quadrivalent uranium. We, therefore, ascertained if there was any photochemical reaction with uranyl-morellin complex in alcohol medium. For this purpose, three samples of the complex solution containing $6{\cdot}368 \times 10^{-5}$ M UO_2^{++} and $3{\cdot}980 \times 10^{-4}$ M morellin were exposed to (1) bright sunlight, (2) diffused daylight and (3) the beam of light in the spectrophotometer at $\lambda = 540$ mμ. In the bright sunlight, the change in transmittance was practically negligible for an exposure of five minutes. But with prolonged exposure (one hour), the transmittance changed from 46·5% to 54·2%. The transmittance, however, remained constant at 46·5% in the case of exposures in diffused daylight and the spectrophotometric beam at 540 mμ, indicating an absence of any photochemical reaction and also the suitability of the conditions employed for the spectrophotometric work on the uranyl-morellin complex in alcohol medium.

Minimum amount of morellin necessary for the estimation of uranium

At 540 mμ, the optical densities of a series of alcoholic solutions, having a morellin to uranium mole ratio of 0·5 : 1 to 9 : 1 were determined. The results are represented in a curve OABC (Fig. 2), which shows that the portion OA of the curve is a straight line up to mole ratio of 2. After this, the rate of change in the optical density gradually diminishes up to mole ratio of 6, beyond which the optical density remains constant. The slow rate of fall in the optical density of the region AB of the curve is due to the dissociation of the complex. For the estimation of uranium, however, the mole ratio of morellin to uranium was maintained at 6 in the subsequent studies.

Effect of the concentration of alcohol on uranyl-morellin complex

When the concentration of ethyl alcohol was below 40%, morellin and its uranium complex got partially precipitated. To prevent such precipitation, the concentration of the alcohol was maintained at 50% or higher, when the optical density remained constant for a given concentration of the complex. In the subsequent work, the concentration of the alcohol was always maintained at 50%.

Effect of pH on uranyl-morellin complex

The influence of pH on the complex was studied to find out the range of pH when uranyl-morellin complex was most stable. pH adjustment of

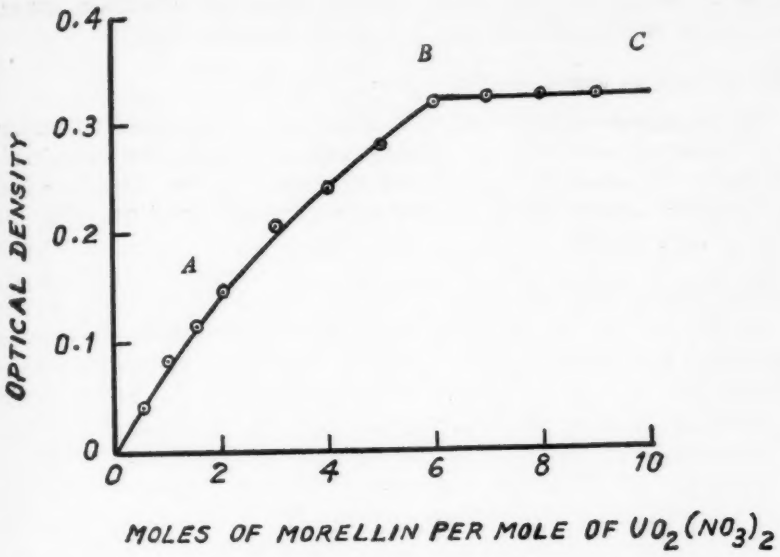


FIG. 2. Variation in Optical Density of the Complex Solution wtih Change in Mole Ratio of Morellin to Uranyl Nitrate.

the complex solution was made by the addition of 0·1 N hydrochloric acid or 0·1 N sodium hydroxide, since the common buffers were found to interfere with the colour or the solubility of the complex. The pH of each of the solutions was determined by means of the glass electrode. The following conclusions were drawn from these studies:

(1) At pH lower than 4·5, the absorption curve of the complex solution was practically identical with that of the morellin solution, showing thereby that the complex is not formed in this pH range.

(2) Beyond pH 7·2, the complex solution gave an absorption maximum at 430 mμ but none at 540 mμ, thus showing again the characteristics of morellin solution in alkaline range of pH. This indicates that the complex is unstable beyond the pH of 7·2.

(3) The uranyl-morellin complex was found stable between pH 5 and 7, giving two characteristic peaks at 430 mμ and 540 mμ. Hence the pH of the solution was always maintained between 5 and 7.

Standard curve for the estimation of uranium

A series of uranyl-morellin complex solutions in 50% alcohol was prepared having different concentrations of uranium, maintaining the mole

ratio of morellin to uranium at 6. Optical densities of these solutions were determined at 540 mμ, employing morellin as a reference solution. The results are given in Fig. 3 A. The curve indicates that the optical density is proportional to the concentration of uranium in two ranges 2 to 6 p.p.m. and 12 to 51 p.p.m., indicating that Beer's law is obeyed in these concentration ranges. The curve is reproducible and it can be used for the estimation of uranium in two sections, 2 to 6 p.p.m. and 12 to 51 p.p.m. The initial straight line of the curve is perhaps due to the slight dissociation of the complex at high dilutions.

Application of differential colorimetry

To apply the method of differential colorimetry for the estimation of uranium, a reference solution was prepared with a concentration of 1·592×

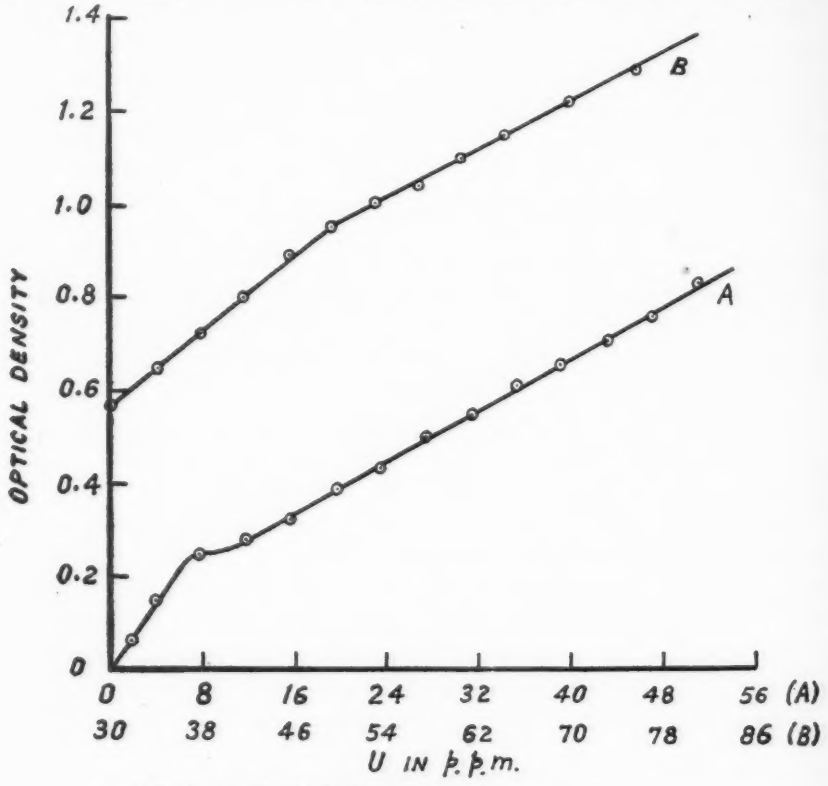


FIG. 3. A. Standard Curve for Uranium.
B. Differential Colorimetry Curve for Uranium.

10^{-4} M with respect to uranium, maintaining the morellin to uranium mole ratio of 6. Employing this solution as standard, optical densities were determined for a series of complex solutions of different concentrations, with the mole ratio of the reagent to uranium at 6. The results are represented in Fig. 3 B, which shows that the plot is not a straight line as required by Beer's law. The curve is, however, reproducible for the conditions described above. Standard curves for known quantities of uranium should, therefore, be constructed for estimation of uranium at higher concentrations.

Interference due to foreign ions

The stock solution of the complex was $2{\cdot}850 \times 10^{-4}$ M with respect to uranium, having a mole ratio of morellin to uranium as 8. 10 ml. of this solution was transferred to a 25 ml. standard flask and mixed with a known amount of a solution of a foreign salt and the volume made up to 25 ml. with 50% alcohol. The optical density of this solution was determined within 15 minutes of mixing. The concentration of the foreign salt in the complex solution was progressively increased till the optical density changed by 2% of the theoretical values. Thus the limiting concentration of the interfering salt was determined (Table I).

TABLE I

Foreign ion	Salt	Ionic ratio tolerated. foreign ion/UO_2^{++}
Ag^+	Nitrate	> 5
Al^{+++}	,,	< 1
Ba^{++}	Chloride	> 5
Ca^{++}	,,	> 5
Co^{++}	,,	< 1
Fe^{+++}	,,	< 1
Hg^{++}	,,	2
K^+	,,	> 10
Mg^{++}	,,	> 5
Mn^{++}	,,	> 5
Na^+	,,	> 10
NH_4^+	,,	> 10
Th^{++++}	,,	< 1
Br^-	Potassium	> 10
Cl^-	,,	> 10
I^-	,,	> 10
NO_3^-	Sodium	> 10

Oxalate, ferrocyanide, thiosulphate, phosphate, fluoride and carbonate interfere even in traces.

Molar composition of the uranyl-morellin complex

(1) *Job's method of continuous variations.*—The composition of the complex was determined by the Job's method of continuous variations,[1] as modified by Vosburgh and Cooper.[12] Optical densities of a series of solutions, prepared by mixing x litres of $8{\cdot}264 \times 10^{-4}$ M morellin solution with $(10 - x)$ litres of $8{\cdot}264 \times 10^{-4}$ M uranyl solution (where x varied from 1 to 10), were determined at 540 mμ, employing morellin solution of the corresponding strength as reference solution. As pointed out earlier, the absorption due to morellin and uranyl solutions is negligible at 540 mμ. Hence the Y function, defined as the difference between the optical density observed for a given mixture of the constituents and the corresponding optical densities of the respective components for no reaction, was taken, in the present case, as the observed optical density of the complex solution. The values of Y are plotted against x in Fig. 4, which shows that the peak in the curve occurs when the mole ratio of morellin to uranyl ions is 6·65 : 3·35,

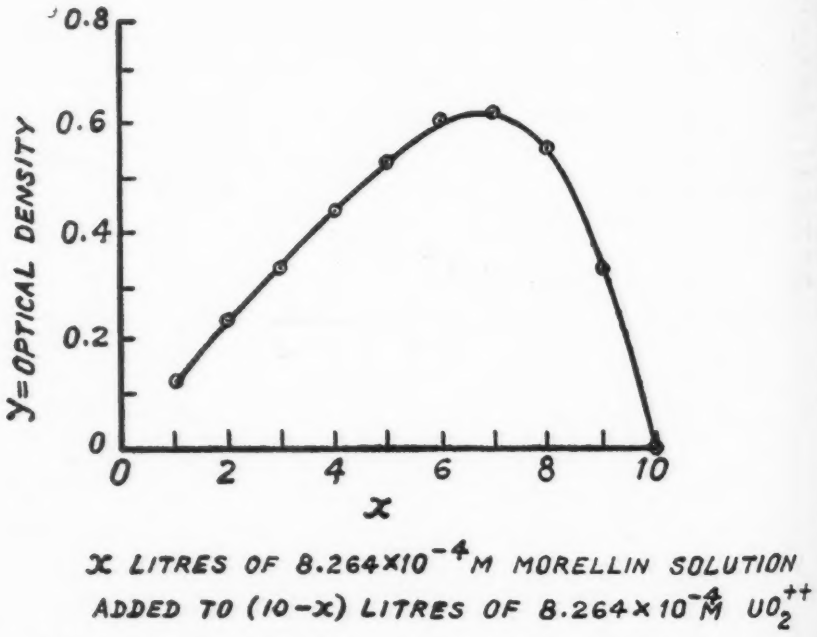


FIG. 4. Molar Composition of the Complex by the Method of Continuous Variations.

i.e., approximately 2 : 1. The complex can, therefore, have the molar composition UO_2M_2, where M is a molecule of morellin.

(2) *Slope ratio method.*—To verify the molar composition of the uranyl-morellin complex, the slope ratio method of Harvey and Manning[13] was also employed. For this purpose, two series of solutions were prepared employing $8{\cdot}264 \times 10^{-4}$ M solutions of morellin and of uranium. In one series, uranium concentration was varied, maintaining morellin constant and in sufficient excess; while in the other, morellin was varied, keeping uranium constant and in sufficient excess. The optical densities of the solutions of both the series were determined at 540 mμ with 50% alcohol as reference. The values obtained are plotted in curves P and Q of Fig. 5. Since the curve P is uneven, only the straight line portion CD was taken into account to find out the slope.

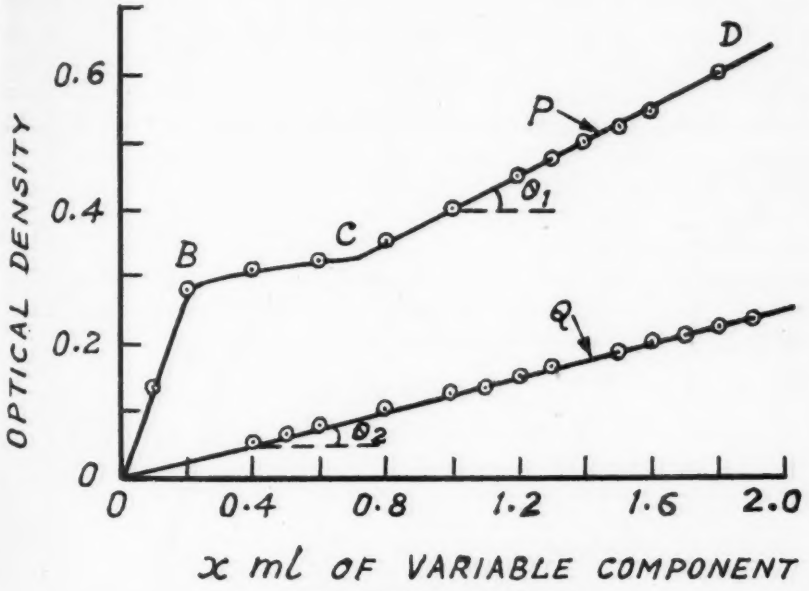


FIG. 5. Curves for Slope Ratio Method.

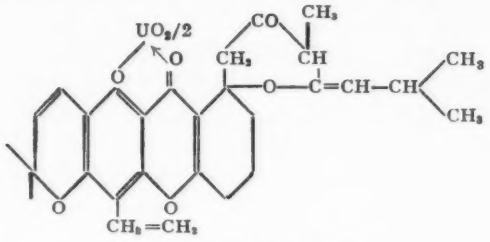
Curve P, *x* ml of Uranyl Nitrate added to 8 ml. of Morellin and finally made to 10 ml. with 50% Alcohol.

Curve Q, *x* ml. of Morellin added to 5 ml. of Uranyl Nitrate and the final volume made to 10 ml. with 50% Alcohol.

Slope of curve P (Portion CD) $= \tan \theta_1 = 0{\cdot}50$

Slope of curve Q $= \tan \theta_2 = 0{\cdot}251$

∴ Molar composition of the complex = 0·50/0·251 = 1·99 (appr. 2)
Thus the slope ratio of the two curves indicates that the molar ratio of morellin to uranyl ion in the complex is 2 : 1, which confirms the findings by Job's method. The complex can, therefore, be represented as the inner complex having 4 co-ordinate uranyl ion, as represented below:



Uranyl-morellin complex

SUMMARY

The spectrophotometric estimation of uranium (VI) has been studied by employing morellin, which forms a reddish brown complex with uranyl solution in ethanol medium. The complex is stable between the pH 5 and 7 and the mole ratio of morellin to uranyl ions in the 4-co-ordinate inner complex of UO_2^{++} radical is 2 : 1. The colour reaction conforms to Beer's law at 540 mμ in two ranges, 2 to 6 p.p.m. and 12 to 51 p.p.m. of uranium. The limits of interference due to some foreign ions during the spectrophotometric estimation of uranium have been determined.

ACKNOWLEDGEMENT

The authors are grateful to Prof. K. R. Krishnaswami and Dr. M. R. A. Rao, for their keen interest and helpful discussion.

REFERENCES

1. Currah, J. E. and Beamish, F. E. — *Ind. Eng. Chem.*, Anal. Ed., 1947, **19**, 609.
2. Crouthomel, C. E. and Johnson, C. E. — *Anal. Chem.*, 1952, **24**, 1780.
3. Hackl, O. .. — *Z. anal. Chem.*, 1940, **119**, 321.
4. Sandell, E. B. .. — *Colorimetric Determination of Traces of Metals*, 1944, p. 433, Interscience Publishers Inc., New York.
5. Davenport, W. H. and Thomason, P. F. — *Anal. Chem.*, 1949, **21**, 1093.
6. Chakrabarty, A. K., Sen, D. and Ray, P. — *J. Ind. Chem. Soc.*, 1953, **30**, 491.

7. Yoe, J. H., Will, F. and Black, R. A. — *Anal. Chem.*, 1953, **25**, 1200.
8. Almássy, G., Nagy, Z. and Straub, J. — *C.A.*, 1955, **49**, 9438.
9. Rao, B. R. L. and Patel, C. C. — *Proc. Ind. Acad. Sci.*, 1955, **42 A**, 317.
10. Bhattacharyya, S. K. and Gulvady, S. — *J. Ind. Chem. Soc.*, 1952, **29**, 649, 659.
11. Job, P. .. — *Ann. Chim.*, 1928, **9** (10), 113.
12. Vosburgh, W. C. and Cooper, G. R. — *J. Am. Chem. Soc.*, 1941, **63**, 437.
13. Harvey, A. E. and Manning, D. L. — *Ibid.*, 1950, **72**, 4488.

STUDIES ON THE KINETICS OF THE DECOMPOSITION OF MUREXIDE IN ACID SOLUTIONS

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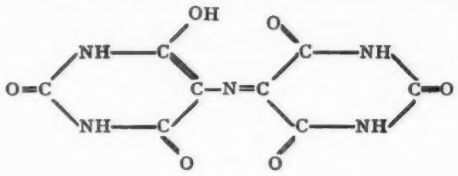
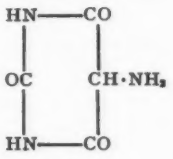
Introduction

In recent years, murexide or ammonium salt of purpuric acid (I) is being extensively used as an analytical reagent for many metallic ions, especially



I

of Ca^{++}. Beck[1] employed murexide for the detection of Sc, Zn, Th and other rare earth and rare metals; Leonid Kul'berg[2] used the same as reagent for heavy metals. Schwarzenbach and Gysling[3] described in detail the use of murexide for quantitative estimation of Ca^{++}. Since then it proved to be an efficient reagent for determination of calcium-content in pharmaceutical products,[4] milk ultra filtrate,[4] etc.[5] Estimation with ease of Ca^{++} in sugar-cane juices is problematical in sugar technological laboratories. During a series of experiments on this investigation employing murexide, a few interesting results on the decomposition of murexide in acid solutions were obtained. It is known[7, 8] that murexide in solutions of low pH undergoes decomposition leading chiefly to the production of uramil (II) and alloxan (III). No data



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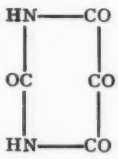

III

exist in the literature on the kinetics of this reaction. The present communication reports for the first time the kinetics of the decomposition of murexide

investigated by employing the characteristic absorption spectra of the substance in the visible region.

Experimental

The commercial (B.D.H.) sample of murexide was purified by the method described by Davidson.[8] One gram of the crude substance was dissolved in 900 c.c. of pure distilled water. The filtrate was salted out with 60 gm. of ammonium chloride. The precipitated substance was washed with absolute methyl alcohol, to be free from chloride and later dried at 120° C., when fine reddish brown crystals possessing a green reflex were obtained.

Absorption spectra of a solution of known concentration of murexide with an equal volume of a buffer solution of desired pH, were studied with Unicam S.P. 350 D.G. spectrophotometer; this last had one cm. effective light path.

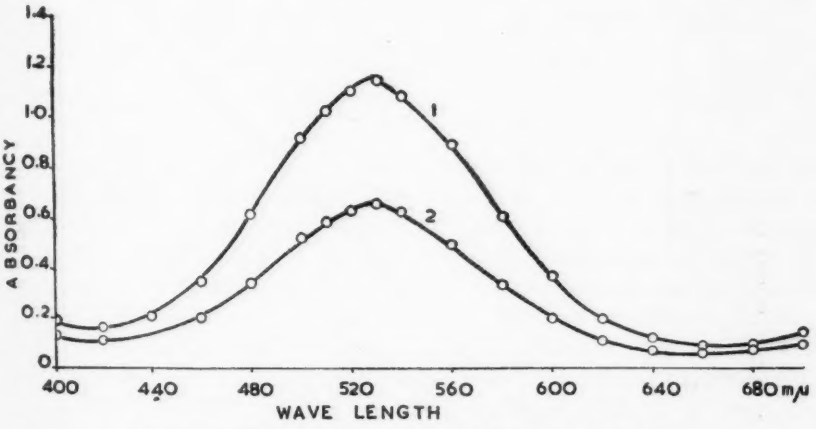

Fig. 1. Absorption Spectra of murexide in the visible region.
(Curve 1 refers to the concentration of 0·125 and Curve 2, to 0·0625 mM of Murexide; pH = 6·0.)

Results and Discussion

A typical series of results on the characteristic absorption spectra of murexide in the range 400 to 700 mμ are given in Fig. 1; in this, curve 1 refers to a concentration of 0·125 mM while curve 2, to 0·0625 mM of murexide at pH = 6·0. It was interesting to note that the absorbancy of murexide increased progressively to a maximum followed by a decrease with increase in the wave-length. Thus, *e.g.*, it was 0·35, 1·13 and 0·2 at $\lambda = 460$,

620 mμ respectively. Murexide has maximum absorption at $\lambda = 530$ mμ in accordance with the data obtained by other workers.[5] Further, this wavelength λ_m was unaffected by a change in the concentration or/and the pH value of the solution.

At a fixed pH, increase of the concentration of the murexide solution especially in the range 10^{-3} to 10^{-6} M enhanced the maximum absorbancy. Thus, *e.g.*, the absorbancy at $\lambda = 530$ mμ was 0·17, 0·65 and 1·13 at 0·016, 0·063 and 0·125 mM of murexide. Further, it was interesting to note that the absorbancy increased sensibly linearly with the concentration (see Fig. 2) in accordance with Beer's law; the corresponding constant had a value of $1{\cdot}04 \times 10^4$ at 25° C. (Table I).

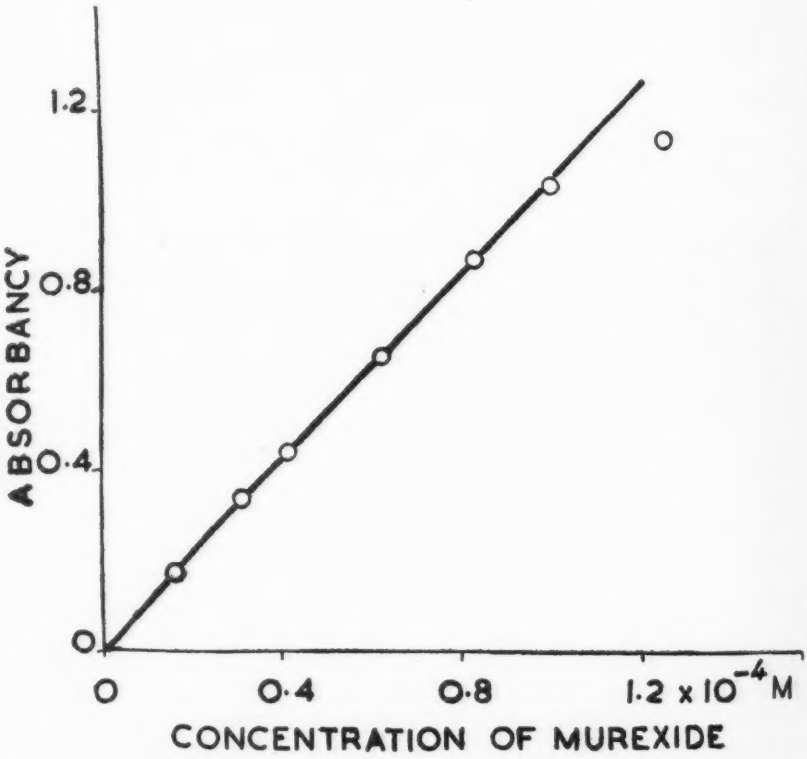

FIG. 2. Variation of absorbancy with the concentration of murexide.
($\lambda = 530$ mμ; pH = 6·0)

TABLE I

Variation of maximum absorbancy at $\lambda = 530\,m\mu$ with concentration of Murexide

Concentration $M \times 10^3$	Optical density	Beer's Constant (10^{-4})
0·125	1·135	0·91
0·10	1·03	1·03
0·0833	0·87	1·04
0·0625	0·655	1·05
0·0417	0·44	1·06
0·0313	0·342	1·09
0·0157	0·171	1·09

Mean Value = 1·04

The data given in Figs. 3 and 4 represent the variation of the absorbancy at $\lambda = 530\,m\mu$ of murexide solution with time, at pH = 2·2 and 2·6 respectively. In these curves 1 and 2 refer respectively to the above data with initial concentrations of 0·125 and 0·0625 mM of murexide. These data were obtained as follows: A known volume of the murexide solution was mixed with equal volume of a buffer and the absorbancy was recorded at different intervals of time at $\lambda = 530\,m\mu$. It was interesting to observe that the absorbancy at $\lambda = 530\,m\mu$ characteristic of the substance decreased progressively with time. Thus for an initial concentration of 0·125 mM and at pH = 2·2, the optical density was 0·72, 0·42 and 0·22 at 1, 5 and 9 min. after the solution was mixed with the buffer. With further increase in time, it decreased to a negligibly small value (see Fig. 3). Essentially similar data were recorded at other pH values (Fig. 4). The decrease with time of the absorbancy was accompanied by the gradual disappearance of the characteristic pink-red colour of the murexide. Furthermore, the above change in the absorption or the colour, appeared permanent and irreversible in the sense that when the acid-reacted solution was made alkaline, the characteristic colour was not restored, and the absorption at $\lambda = 530\,m\mu$ was not exhibited. This is illustrated clearly by the data given in Figs. 5 and 6; these refer to the experiments in which during the progress of the reaction, the

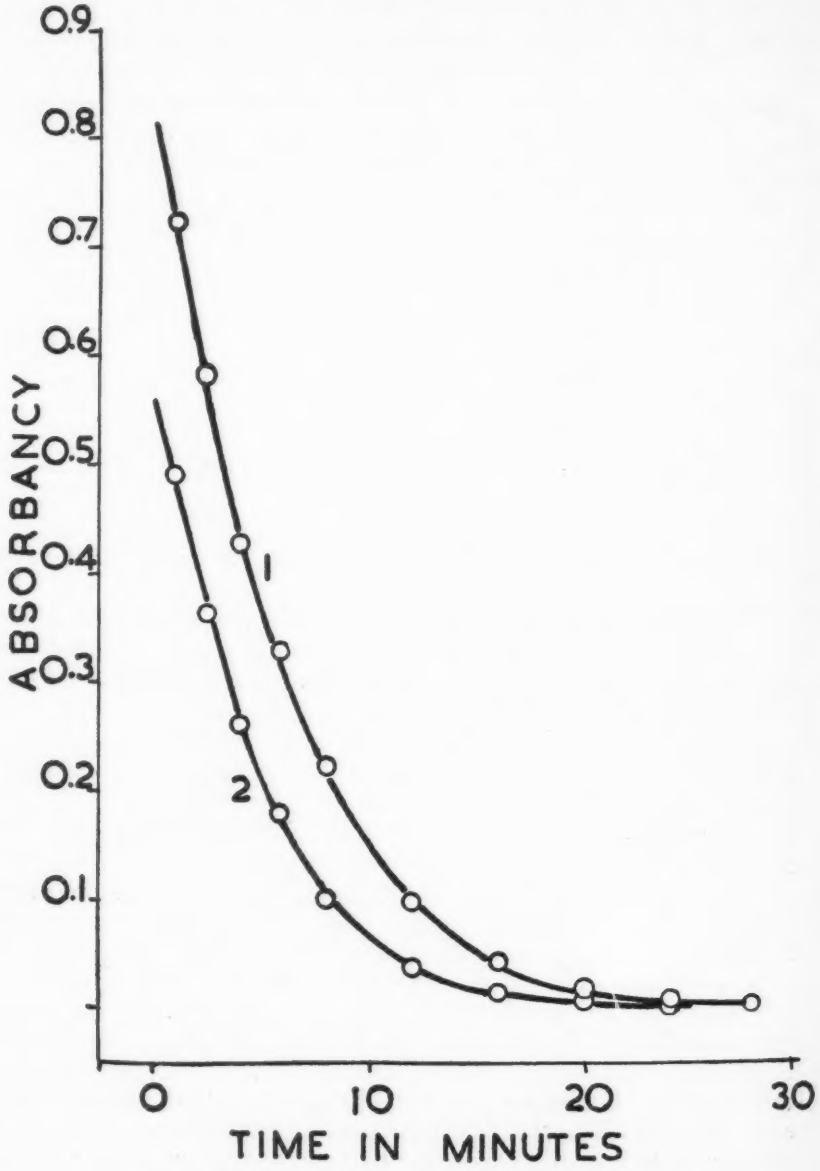

FIG. 3. Decomposition of murexide with time at pH = 2·2.
(Curve 1 = 0·125 and Curve 2 = 0·0625 mM of murexide ; λ = 530 mμ)

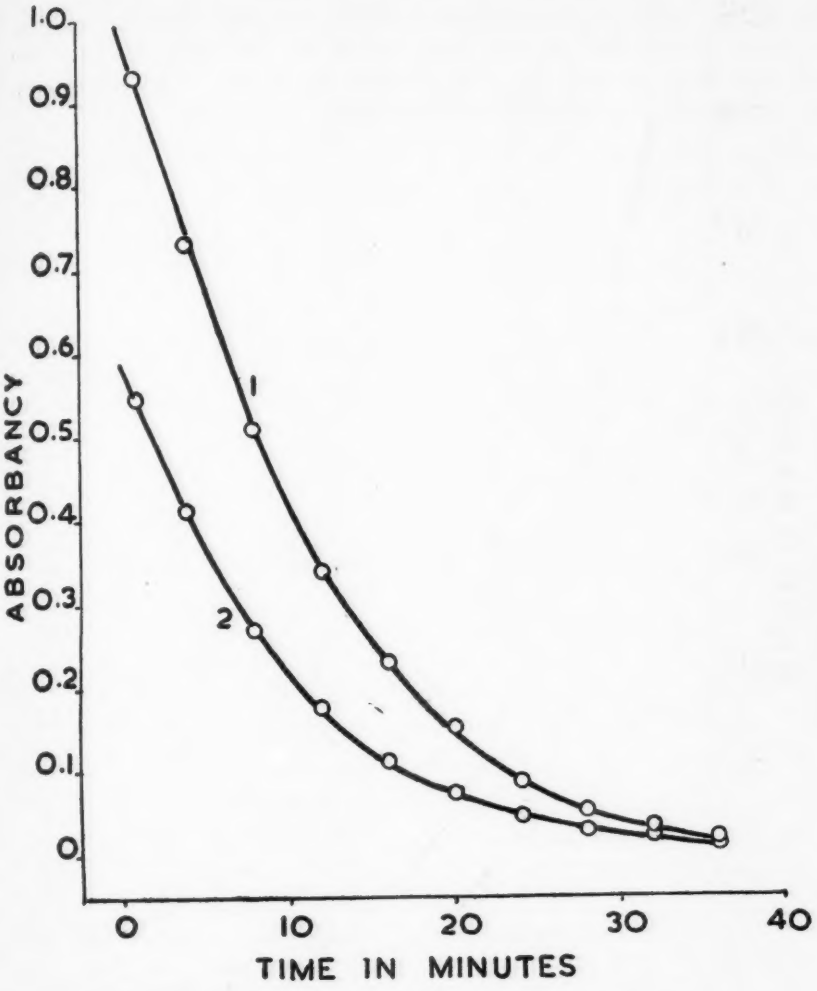

FIG. 4. Decomposition of murexide with time at pH = 2·6.
(Curve 1 = 0·125 and Curve 2 = 0·0625 mM of Murexide; $\lambda = 530$ mμ)

pH of the solution has been increased to 8 by addition of 0·2 c.c. of 4 N sodium hydroxide solution, which caused negligible dilution of the murexide solution. It was interesting to note that as soon as the pH was raised, the reaction leading to the decrease in the absorbancy of murexide was quenched as evidenced by the observation that the absorbancy of the solution recorded

just before addition of alkali remained later sensibly constant (see Figs. 5 and 6). These data not only demonstrate the irreversible nature of the decomposition, but also reveal the marked dependence of the reaction on the hydrogen-ion concentration of the solution.

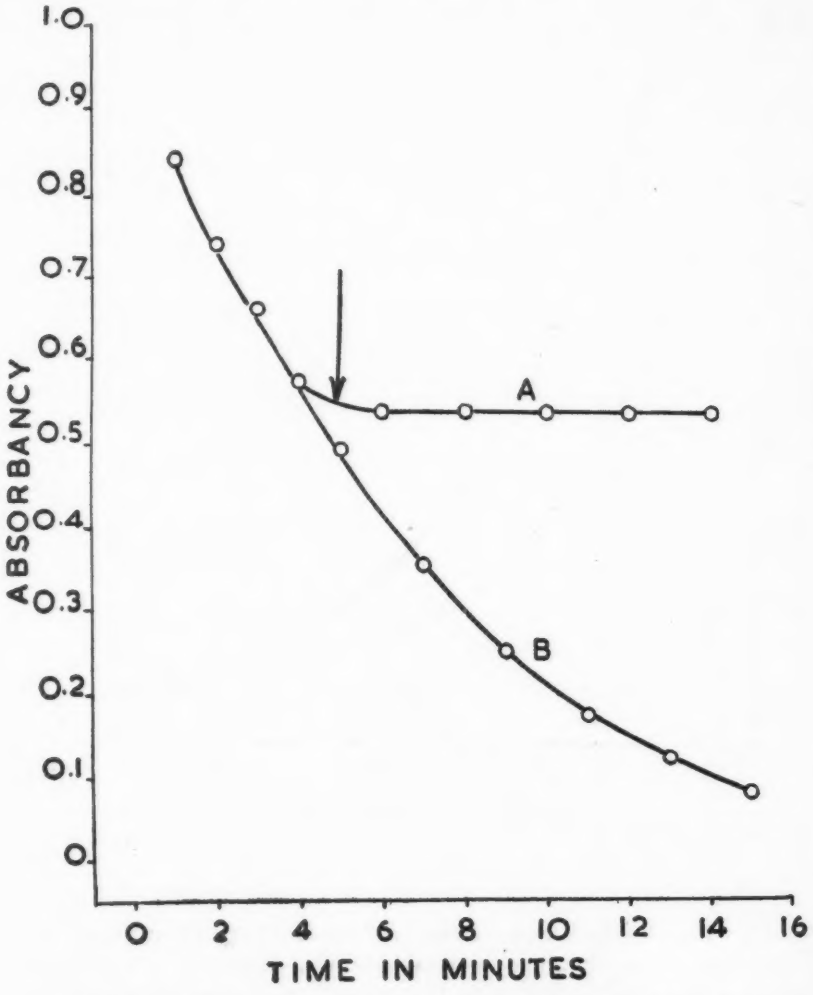

FIG. 5. Effect of addition of alkali to the acid reacted murexide solution.
[Initial pH of the solution = 2·2 (Curve B), pH after addition (at the instant indicated by the arrow) of the alkali = 8·0 (Curve A). λ = 530 mμ.]

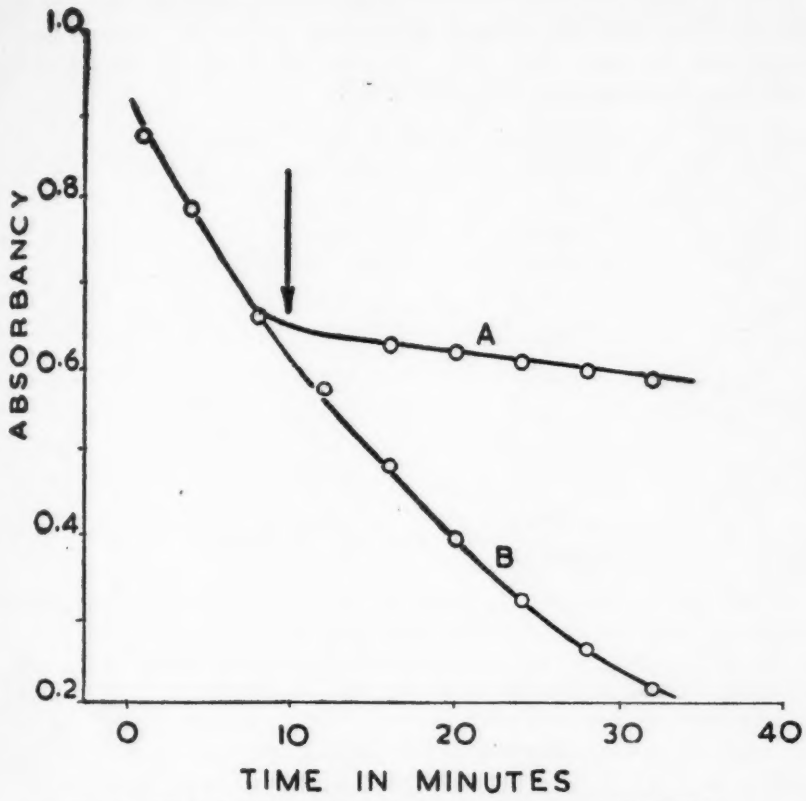

FIG. 6. Effect of addition of alkali to the acid reacted murexide solution.
[Initial pH of the solution = 2·8 (Curve B), pH after addition (at the instant indicated by the arrow) of the alkali = 8·0 (Curve A). λ = 530 mμ.]

The data in Figs. 3 and 4 further show that larger the pH of the solution, the greater is the time necessary for complete decomposition of a known concentration of murexide. Thus the absorbancy at $\lambda = 530$ mμ decreased to undetectably small value within 25 min. at pH = 2·2 (curve 1, Fig. 3), while the same at pH = 2·6 decreased to zero value by about 40 min.

Table II gives the results on the time necessary for half decomposition of a known initial concentration of murexide, recorded at different pH values. These were employed for the determination of the order (n) of the reaction under investigation. The figures in the last column gave an average value of 0·93 or ~ 1 for n. It is for this reason that the authors considered the

reaction to be roughly first order in nature and presumably similar to the acid hydrolysis, inversion of cane sugar, etc.

TABLE II

Determination of the order of reaction
$C_1 = 0{\cdot}125\ mM$ *and* $C_2 = 0{\cdot}0625\ mM$ *of Murexide*

pH	Time for half decomposition of C_1 ($t^1_{\frac{1}{2}}$)	Time for half decomposition of C_2 ($t^2_{\frac{1}{2}}$)	Order of reaction (n)
2·2	4·25	3·625	0·96
2·4	6·625	5·125	0·93
2·6	8·25	7·0	0·96
2·8	17·0	12·0	0·91

There are several methods employed for calculating the first order rate constant k_1 from the readings r at time t of some physical property characteristic of the substance undergoing reaction, and proportional to the concentration thereof. Since the variation of the absorbancy of murexide solution obeys roughly Beer's law (Table I, Fig. 2), it has been felt that the same could be satisfactorily utilised for obtaining the value of k_1. For this purpose, the authors employed the following equation due to Guggenheim.[9]

$$\log (r' - r) = a - k_1 t$$

where r' is a reading at time $t + \tau$, where τ is a chosen constant interval; and a, a constant. The remarkable simplicity of this equation is that it is only necessary to plot $\log (r' - r)$ against t and measure the slope of the line thus obtained, which gives directly the value of the first order rate constant. Fig. 7 shows one of the typical lines thus obtained by the application of the above formula to the data given in Fig. 3 (Curve 1). This gave a value of $7{\cdot}98 \times 10^{-6}$ min.$^{-1}$ (25° C.) for k_1 for an initial concentration of 0·125 mM of murexide at pH = 2·2.

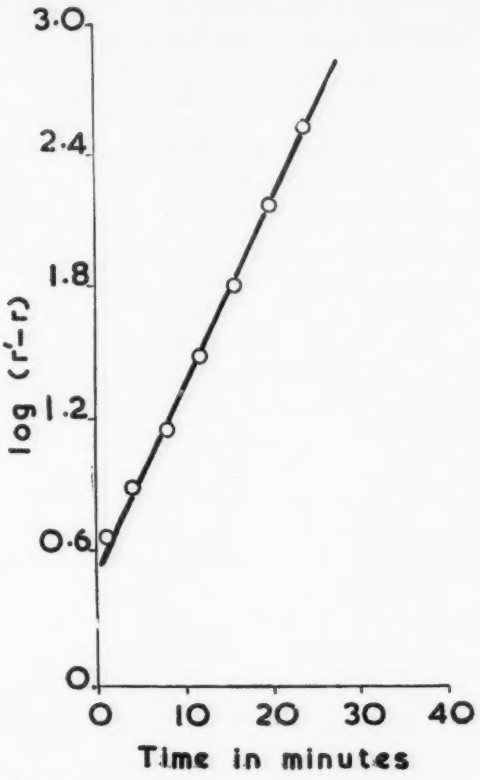

FIG. 7. Determination of the first order rate constant.
(pH = 2·2 ; concentration = 0·125 mM; λ = 530 mμ)

SUMMARY

Decomposition of murexide in solutions of low pH (2–6) has been investigated spectrophotometrically. At pH < 6, the characteristic absorption of of murexide at $\lambda = 530$ mμ decreased irreversibly with time, following first order law; the corresponding rate constant k_1 had a value of $7{\cdot}98 \times 10^{-6}$ min.$^{-1}$ (25° C.) for an initial concentration of 0·125 mM of murexide at pH = 2·2.

ACKNOWLEDGEMENT

Authors' grateful thanks are due to Professor K. S. G. Doss, D.SC., F.R.I.C. (Lond.), F.INST.P., F.A.SC., Director, Indian Institute of Sugar Technology, anpur, for his kind interest and valuable encouragement in the work.

REFERENCES

1. Beck, G. .. *Anal. Chim. Acta*, 1947, **1**, 69.
2. Leonid Kul'berg .. *J. Gen. Chem. U.S.S.R.*, 1947, **17**, 1089.
3. Schwarzenbach, G. and Gysling, H. *Helv. Chim. Acta*, 1949, **32**, 1314.
4. Flaschka, H. .. *Scientia Pharma*, 1953, **21**, 126.
5. Smeets, W. Th. G. M. .. *Nature*, 1952, **169**, 802.
6. Flaschka, H. .. *Textile Rundschau*, 1954, **9**, 77; see also Parrish, J. R., *Proc. Internat. Soc. Sugarcane Tech.*, 1953, 742.
7. Heilbron, T. and Bunbury, H. *Dictionary of Organic Compounds*, Eyre & Spottiswoode, London, 1946, **3**, 547.
8. Davidson, D. .. *J. Amer. Chem. Soc.*, 1936, **58**, 1821.
9. Guggenheim, E. A. .. *Phil. Mag.*, 1926, **2**, 538; *cf.*, Bond, W. N., *Probability and Random Errors*, Longmans, Green & Co., London, 1935, 112. This method due to Bond is combursome and is not applied here.

POLAROGRAPHIC STUDIES OF MUREXIDE—I

By N. A. Ramaiah and Vishnu

(Department of Physical Chemistry, Indian Institute of Sugar Technology, Kanpur)

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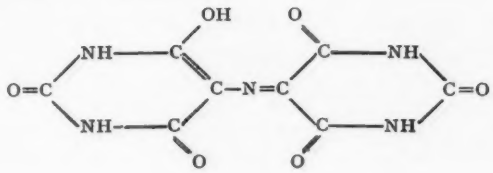
Introduction

Since the discovery of polarography by Heyrovski it has been extensively employed for qualitative detection and quantitative analysis of electro-oxidisable or reducible substances. In recent years, it has proved to be an efficient method for investigation of oxidation-reduction equilibria, keto-enolic tautomerism, etc., of a number of organic substances. Thus Sartori and Liberti[1] studied the oxidation-reduction of alloxan-dialuric acid; and Smith and Waller[2] examined the equilibrium of nitrosobenzene-N-phenyl-hydroxylamine. Muller and Baumberger[3] investigated the keto-enolic equilibrium of quinol and benzoquinone system. Polarographic technique is also found to be very useful in understanding the electro-chemical oxidation and reduction mechanism especially the number of electrons involved therein and the reversible or irreversible nature thereof. The reduction of formaldehyde at the dropping mercury electrode was found to take place according to the following mechanism[4]:

$$HCHO + 2e + 2H^+ \rightarrow CH_3OH$$

Distinction between reversible and irreversible organic reductions is also brought out from polarographic analysis. In a reversible oxidation-reduction system, the half-wave potential for the oxidation of the reductant is identical with that for the reduction of the oxidant; and is equal to the potentiometrically determined normal potential of the system.[5, 6] The two, reversible and irreversible, processes are controlled by equations involving different and characteristic quantities (*vide infra*).

The present investigation deals with polarographic studies of murexide or ammonium salt of purpuric acid



This substance has been widely used as an indicator for metal ions, especially of Ca^{++}.[7, 8] Thus Beck[9] employed murexide as an analytical reagent for Sc, Zn, Th and other rare earth metals; Engel[10] used the same for titrimetric determination of Ca^{++} and Mg^{++}. And, Oestertag and Rinck[11] studied the colorometric estimation of Ca^{++} with the aid of murexide. Smeets and Seekles[12] determined spectrophotometrically the content of Ca^{++} in milk-ultrafiltrate. Murexide was also employed for analytical work in pharmaceutical[13] and textile[14] products. During a series of trials for estimation with murexide of the calcium content in sugarcane juices, it appeared desirable to investigate in detail the polarography of murexide, the knowledge of which would be of utility for development of ampereometric titrations with murexide.

EXPERIMENTAL

The commercial (B.D.H.) sample of murexide was purified according to the method described by Davidson[15]; this method was found to give 99–100% purity.[16] One gram of the substance was dissolved in 900 c.c. of pure twice distilled water and the filtered solution was salted out with ammonium chloride. The precipitated substance was washed several times with absolute methyl alcohol and later dried at 120° C.

0·1 N potassium chloride (Analar quality) solution was used as the supporting electrolyte. The dissolved air in the solutions was removed by bubbling purified nitrogen. 0·5% of gelatin was used as the maximum suppressor.*

The polarograms at different concentrations of murexide were obtained by a manual polarograph set up in this Laboratory. The following were the characteristics of the capillary of the dropping mercury electrode in 0·1 N potassium chloride solution with open circuit:

$$\text{Mass of the drop} = 3{\cdot}23 \text{ mg.}$$

$$\text{Drop time} = 1{\cdot}64 \text{ sec.}$$

A pool of mercury at the bottom of a cell (capacity 100 ml.) served as the other electrode. D.C. potentials obtained from a potentiometer and applied to the dropping mercury electrode (used as cathode in this investigation) and mercury pool, could be read accurately up to 1 millivolt. The current flowing through the system was measured as follows: A suitable carbon resistor was introduced serially into the circuit; the potential developed across the same due to the passage of the current was measured by a Leeds and Northrup

* Murexide exhibits a pronounced positive maximum; the details of the effect of maximum suppressors like gelatin, methyl red, etc., will be reported in a later communication.

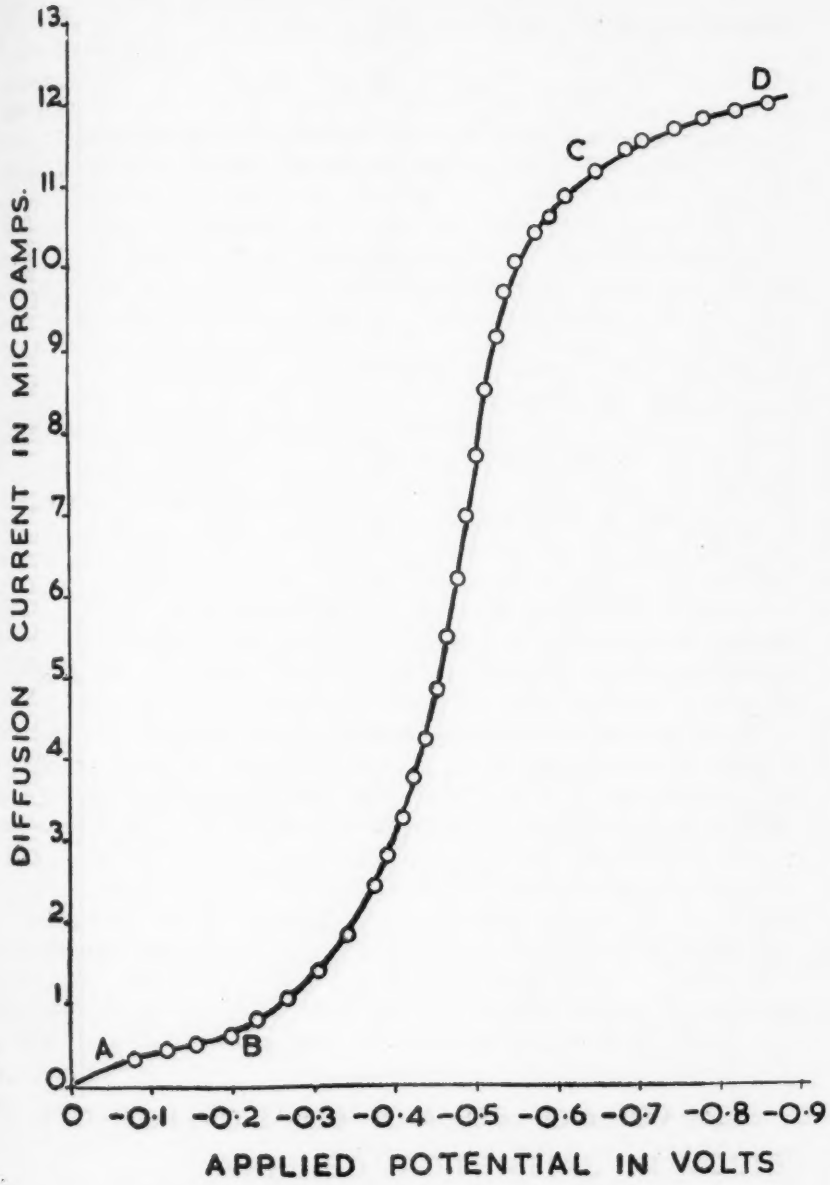


FIG. 1 Polarogram of murexide in 0·1 N KCl solution.

potentiometer; the accuracy of the measurement was 0·5 of a millivolt, which corresponded to 0·05 of a microampere.

RESULTS AND DISCUSSION

Figure 1 gives a typical series of results representing the variation of the current i with potential E applied to the dropping mercury electrode; the data refer to a concentration of 1·4 mM of murexide (at neutral pH). When the dropping mercury electrode was made progressively negative, at low applied potentials only a minute current could be recorded (AB, Fig. 1). When the potential was increased beyond a characteristic value corresponding to the decomposition potential, marked increase in i, tending to saturation at large values of E, was noticed. Examination of the data in Fig. 1 shows clearly that as for the other reducible substances, the results for murexide gave characteristic S-shaped curves usually known as the polarograms. Further, it may be noted that the polarogram was poorly " defined" in the sense that the portions representing the residual current (portion AB) and limiting current (CD, Fig. 1) were not parallel to the voltage-axis, as is to be expected from theoretical considerations. This was primarily due to the low concentrations of murexide employed in the present investigation. Use of larger concentrations met with the difficult circumstance of salting out of the substance by the supporting electrolyte (KCl). At low concentrations, the appreciable rate of change of *condenser* current with the applied voltage led to the observation of progressively increasing limiting currents (Fig. 1). When the residual current was corrected for, well-defined curves could be obtained at all concentrations studied; a few of the typical series of these results are given in Fig. 2. In this, curves 1–4 refer respectively to 0·8, 1·0, 1·2 and 1·4 mM of murexide. It was interesting to note that the diffusion current (i_d) decreased progressively with a reduction in the concentration of murexide. Thus, *e.g.*, i_d was 10·3, 8·6 and 7·4 μamp. at 1·4, 1·2 and 1·0 mM of murexide. With concentration C, i_d increased roughly linearly (see Fig. 3) in accordance with Ilkovic's equation.[6] Further, the half-wave potential ($E_{\frac{1}{2}}$) characteristic of the electro-active substance was −0·38 volts *vs.* S.C.E. for murexide in 0·1 N KCl solution; it was not sensibly affected by a change in the concentration of the substance (see inset, Fig. 2). These data indicate clearly that murexide is reducible at the dropping mercury electrode.

Kuhn and Lyman[17] investigated the reduction of murexide with $Na_2S_2O_4$ and observed that reduction of one molecule of murexide required 2 atoms of H, leading to the production of a leuco-compound.

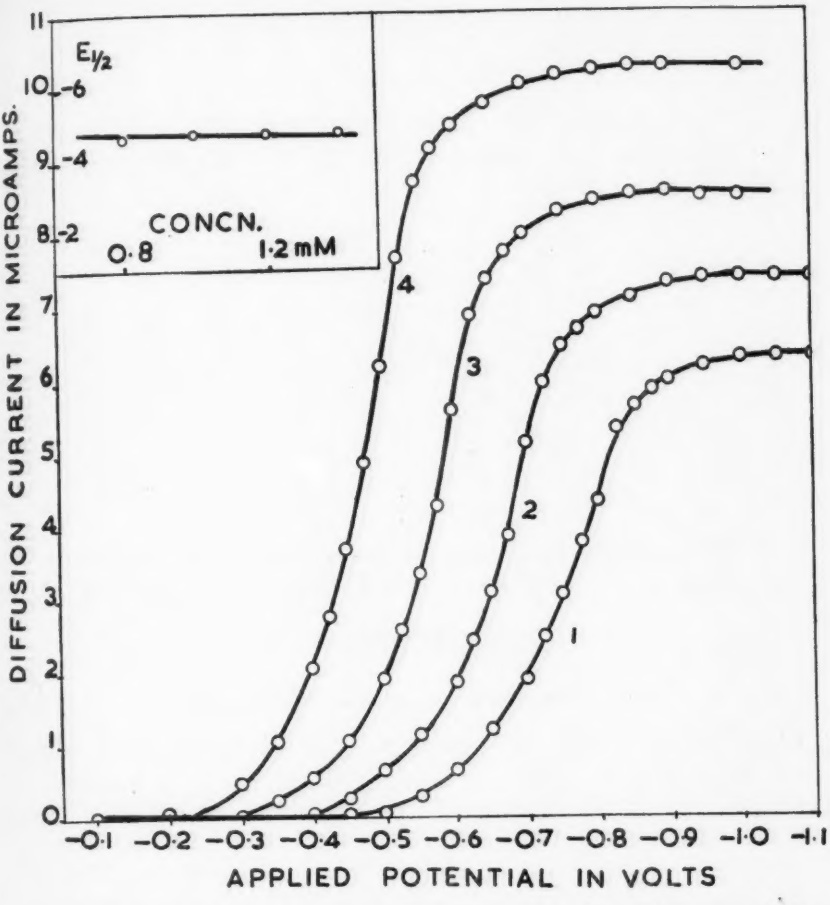


FIG. 2. Reduction of murexide at the dropping mercury electrode. at different concentrations. The potential scale for curve 4 is marked on the abscissa; the other curves have been shifted progressively to the right by 0·1 volt.

Heyrovsky and Ilkovic[18, 19] deduced the following equations for reversible and irreversible reduction processes occurrent at the dropping mercury electrode:

$$E = E_{\frac{1}{2}} - \frac{0{\cdot}0591}{n} \log (i/i_d - i) \qquad \text{(reversible)}$$

$$E = E_{\frac{1}{2}} - \frac{0{\cdot}0591}{a} \log (i/i_d - i) \qquad \text{(irreversible)}$$

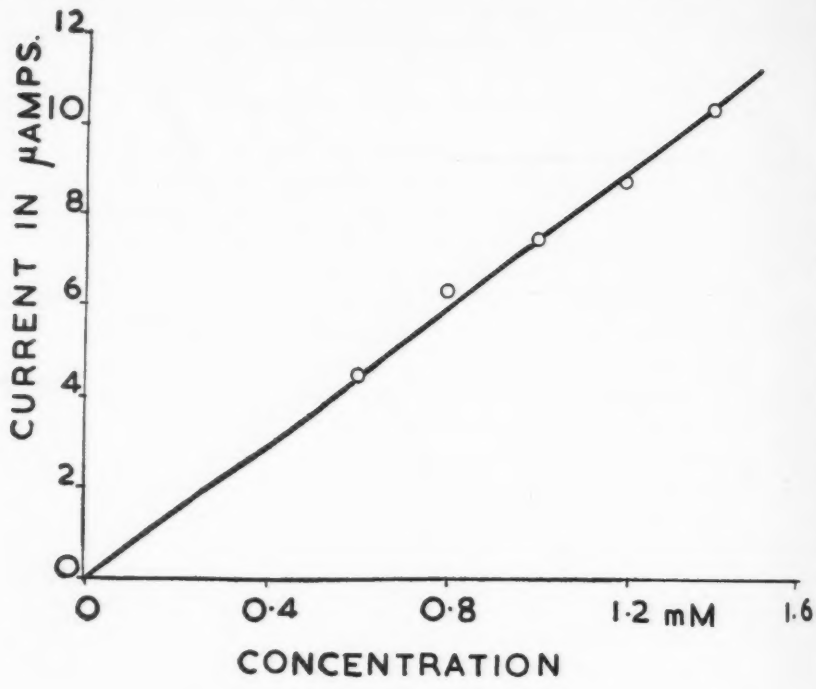


FIG. 3. Effect of concentration on the diffusion current i_d.

where n is the number of electrons involved in the reversible reduction process; and α also contains a factor related to the rate constant of a slow reaction responsible for the irreversible nature of the reduction. In the former equation, n is always an integer and is equal to or greater than unity while in the equation for irreversible process α is found very often, though not invariably, to be less than one. Both these equations require that $E_{\frac{1}{4}}$ should be constant and independent of the concentration of the electroactive substance (*vide supra*); and that the plots log $(i/i_d - i)$ *vs.* E should be linear. It is instructive to consider from the data in Fig. 4 that for the reduction of murexide at the dropping mercury electrode, log $(i/i_d - i)$ varies roughly linearly with applied potential, E. The slope of the line was, approximately, 0·5 (*cf.* also Table I), leading to the deduction that the reduction of murexide at the dropping mercury electrode is irreversible in nature.

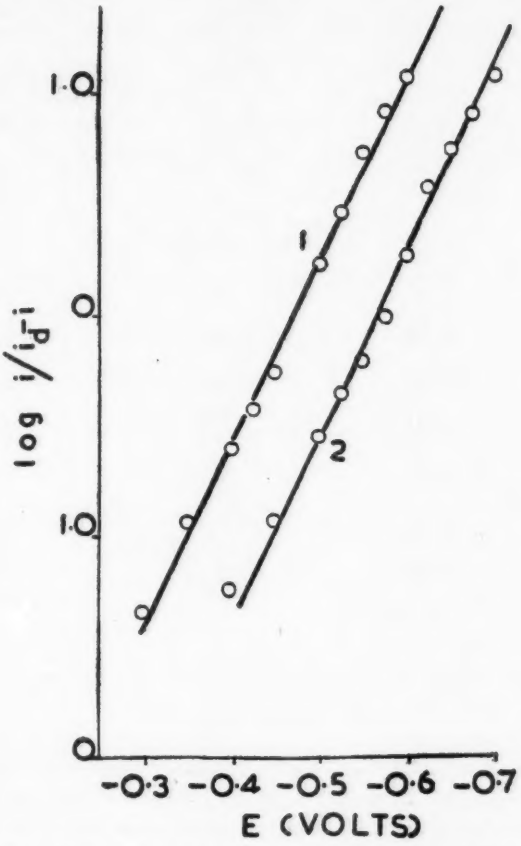


FIG. 4. Variation of log i/i_d-i with applied potential E.

TABLE I

Applied potential E (volts)	Concentration = 1·4 mM			Concentration = 1·2 mM		
	i (μA)	$\log (i/i_d - i)$	α	i (μA)	$\log (i/i_d - i)$	α
− 0·300	0·50	− 1·29	0·43	·55	−1·17	0·39
− 0·350	1·05	− 0·94	0·44	1·04	−0·87	0·40
− 0·400	2·05	− 0·60	0·46	1·89	−0·56	0·42
− 0·425	2·80	− 0·43	0·48	2·58	−0·37	0·42
− 0·450	3·68	− 0·26	0·54	3·36	−0·20	0·42
− 0·500	6·46	+ 0·23	0·61	5·62	+0·26	0·70
− 0·525	7·67	0·46	0·58	6·89	0·58	0·73
− 0·550	8·72	0·74	0·60	7·40	0·76	0·62
− 0·600	9·50	1·07	0·52	8·03	1·09	0·52
			Mean 0·52			Mean 0·52

$E_{\frac{1}{2}}$ = 0·478 Volts; i_d for C = 1·4 mM was 10·30 μA; and i_d for C = 1·2 mM was 8·69 Aμ.

SUMMARY

Reduction of murexide at the dropping mercury electrode was investigated. Data obtained at different concentrations in the range 0·5–2 mM showed that the half-wave potential of murexide was − 0·38 volt *vs.* S.C.E. in 0·1 N KCl solution (neutral pH) and was not altered with concentration; with this last, the diffusion current increased linearly. Analysis of the plots $\log (i/i_d - i)$ *vs.* E indicated that the reduction was irreversible in nature.

ACKNOWLEDGEMENT

Authors' grateful thanks are due to Professor K. S. G. Doss, D.Sc., F.R.I.C., F.INST.P., F.A.SC., Director, Indian Institute of Sugar Technology, Kanpur, for his kind interest in the work.

REFERENCES

1. Sartori, G. and Liberti, A. *Ric. Sci.*, 1946, **16**, 313.
2. Smith, J. W. and Waller, J. G. *Trans. Farad. Soc.*, 1950, **46**, 290.

3. Muller, O. H. and Baumberger, J. P. *Trans. Electrochem. Soc.*, 1937, **71**, 181.
4. Jahoda, F. G. .. *Coll. Czech. Chem. Comn.*, 1935, **7**, 415.
5. Page, J. E. .. *Quarterly Reviews*, Chemical Society, London, 1952, **6**, 277.
6. Kolthoff, I. M. and Lingane, J. J. *Polarography*, Interscience Publishers, 1952.
7. Kulberg, L. .. *J. Gen. Chem., U.S.S.R.*, 1947, **17**, 1089.
8. Schwarzenbach, G. and Gysling, H. *Helv. Chim. Acta*, 1949, **32**, 1314.
9. Beck, G. .. *Anal. Ghim. Acta*, 1947, **1**, 69.
10. Engel, O. .. *Das Leder*, 1951, **2**, 241.
11. Ostertag, H. and Rinck, M. E. *Chim. Anal.*, 1952, **34**, 108.
12. Smeets, W. Th. G. M. and Seekles, L. *Nature*, 1952, **169**, 802.
13. Flaschka, H. .. *Scientia Pharma.*, 1953, **21**, 126.
14. ———— .. *Textile Rundschau*, 1954, **9**, 77.
15. Davidson, D. .. *J. Amer. Chem. Soc.*, 1936, **58**, 1821.
16. Moser, J. H. and Williams, M. B. *Anal. Chem.*, 1954, **26**, 1167.
17. Kuhn, R. and Lyman, J. C. *Ber.*, 1936, **69 B**, 1547.
18. Heyrovsky, J. and Ilkovic, D. *Coll. Czech. Chem. Comn.*, 1935, **7**, 198.
19. *Cf.* Ref. 6, p. 195.

THE GREAT SOLAR FLARE OF FEBRUARY 23, 1956 AND ASSOCIATED IONOSPHERIC EFFECTS AT AHMEDABAD

By K. R. Ramanathan, F.A.Sc., R. V. Bhonsle, K. M. Kotadia and R. G. Rastogi

Received April 27, 1956

For some months now, the Physical Research Laboratory, Ahmedabad, has been recording continuously cosmic radio noise from the vertical sky on a frequency of 25 Mc/s, using a broadside collinear array of 16 dipole aerials, covering an angle of 37° in N-S and 30° in E-W directions. A Hammerlund Communications receiver with its output amplified by a differential D.C. amplifier, and calibrated by a diode noise generator, is used to record the noise intensity on an Evershed recording milliammeter. On 23–2–1956, an exceptionally large sudden absorption of cosmic noise (SCA) was observed. It commenced at 0831 hours 75° E Meridian Time, (0331 hours G.M.T.), reached its maximum at 0838 hours and died out by about 0930 hours. The sudden increase in absorption took place in two stages, the second and larger increase being at 0833 hours. A photograph of the record is reproduced in Fig. 1.

2. In Fig. 2, the noise record of 23–2–1956 is compared with those on three neighbouring days. By interpolating the "undisturbed" curve of variation on 23–2–1956, and expressing the differences in intensity at different times from the undisturbed values, it appears that the intensity of cosmic noise at the time of maximum absorption was 6·5 decibels below normal. This value may be compared with the highest absorption of 7 db. noted by Dr. C. A. Shain and Dr. A. P. Mitra (1954) at 18·3 Mc/s during a solar flare on April 20, 1951, in Australia.

3. By the courtesy of the Chief Engineer, Overseas Communication Service, India, we give below the observations on the fade-outs of long-distance communication recorded by the Beam Wireless Station, Poona, on 23–2–1956.

Table I

Radio-communication fade-outs recorded by Beam Wireless Station, Poona, on 23–2–1956

Circuit	Frequency (Kc./s.)	Time of Fade-out
Osaka, Japan	18,355	0835 to 1015 hours
China	20,120	75° EMT. Weak signals
Melbourne	18,700	Up to 1045 hours
Bangkok	18,200	
Indonesia	18,135	0835 to 1915 hours
Kabul	7,788	0835 to 1915 hours

ERRATUM

Vol. XLIII, No. 5, May 1956

On page 306, Table I, Time of Fade-out in the Circuit to Indonesia and Kabul *should read as* "0835 to 1015 hours" *instead of* "0835 to 1915 hours".

CURRENT MA

The equivalent vertical incidence frequencies for one- or two-hop reflections for an assumed height of reflection of 300 km. are all below 7 Mc/s.

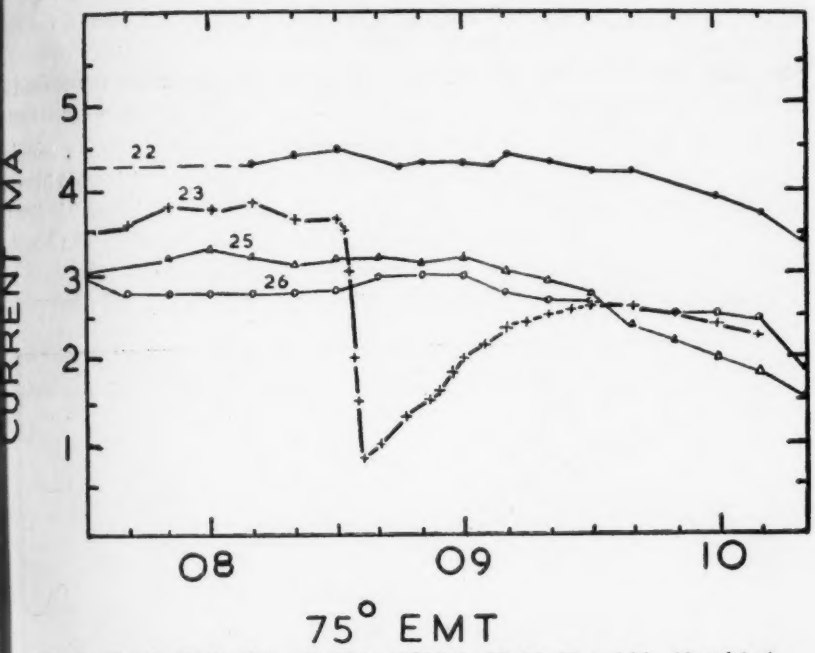


Fig. 2. Cosmic Radio Noise, 25 Mc/s, 1956 Feb. 22, 23, 25 and 26, Ahmedabad.

4. The hourly records of the vertical pulse soundings of the ionosphere made in the laboratory showed that the reflections were normal at 0800 hours 75° EMT, but at 0900 hours, there was a black-out of all vertical reflections up to 10 Mc/s (Fig. 3). It will be seen that at the same hour, the reflections of radio waves emitted by broadcasting stations were not visible even at 15 Mc/s.

All this, and most significant of all, the definite significant increase in cosmic-ray meson flux recorded at the low geomagnetic latitudes of Ahmedabad, Kodaikanal and Trivandrum, mark out this solar flare as one of exceptional magnitude and character (*Ibid.*, Sarabhai *et al.*).

5. It is known that these sudden short-wave absorptions (SCA's) follow solar flares and are associated with sudden changes of ionospheric reflections of long radio waves and magnetic "crotchets". The Cavendish workers (Bracewell, 1952; Weekes, 1955) give reasons for thinking that the additional

short-wave absorption occurs in a layer well below the normal E layer, at a height of about 75 km. They have made the suggestion that during strong flares, the sun emits some radiation (probably in the short X-ray region) which penetrates the F and E layers and ionises some constituent of the atmosphere which exists normally in small quantities at about 75 km. Nothing, however, is *definitely* known either about the frequency of the radiation or the atmospheric constituent reponsibile for the increased low-level ionisation.

6. It may be of some interest to record here another strong cosmic radio absorption which occurred on 10–3–1956. It commenced at 0945 hours, reached its peak at 1005 hours and died out at about 1110 hours 75° EMT (Fig. 4). The maximum absorption in this instance was 3·6 db. The hourly ionospheric vertical soundings at Ahmedabad showed normal reflections at 0850 hours, complete absorption up to 9 Mc/s at 0955 hours and absorption

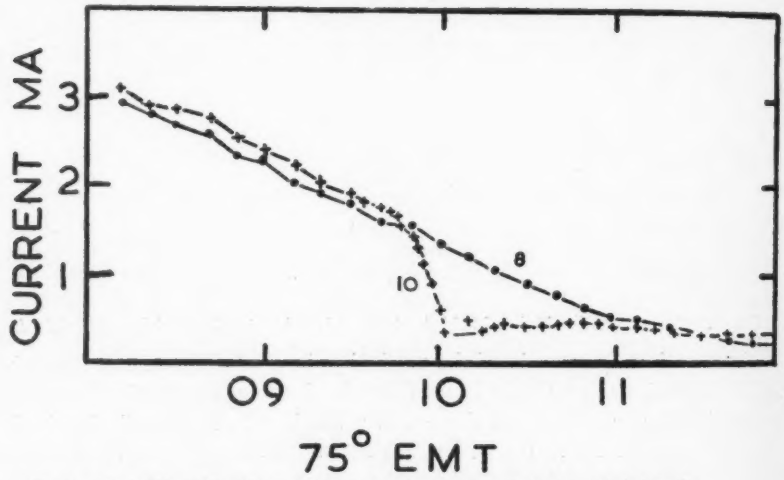


FIG. 4. Cosmic Radio Noise, 25Mc/s, 1956 March 8 and **10**, Ahmedabad.

up to 5 Mc/s at 1055 hours. No cosmic ray effects were observed at Indian latitudes.

As we are now on the up-grade of solar activity, more flares of varying degrees of intensity may be expected in the next two or three years and careful monitoring of all the phenomena associated with them, will be of great value.

REFERENCES

Shain, C. A. and Mitra, A. P. .. *J. Atmosph. Terr. Phys.*, 1954, **5**, 316.
Bracewell, R. N. .. *Ibid.*, 1952, **2**, 226.
Weekes, K. .. *Observatory*, Geophysical Discussion, 1955, **75**, 61.

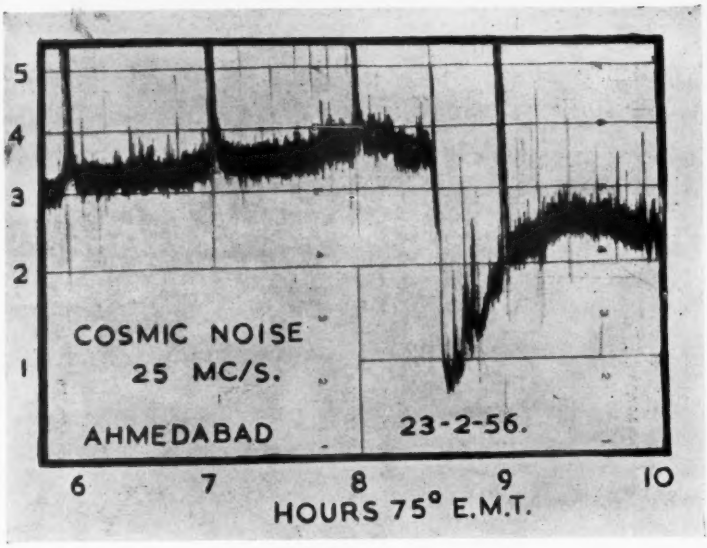

5
4
3
2
1
COSMIC NOISE
25 MC/S.
AHMEDABAD
23-2-56.
6
7
8
9
10
HOURS 75° E.M.T.

FIG. 1

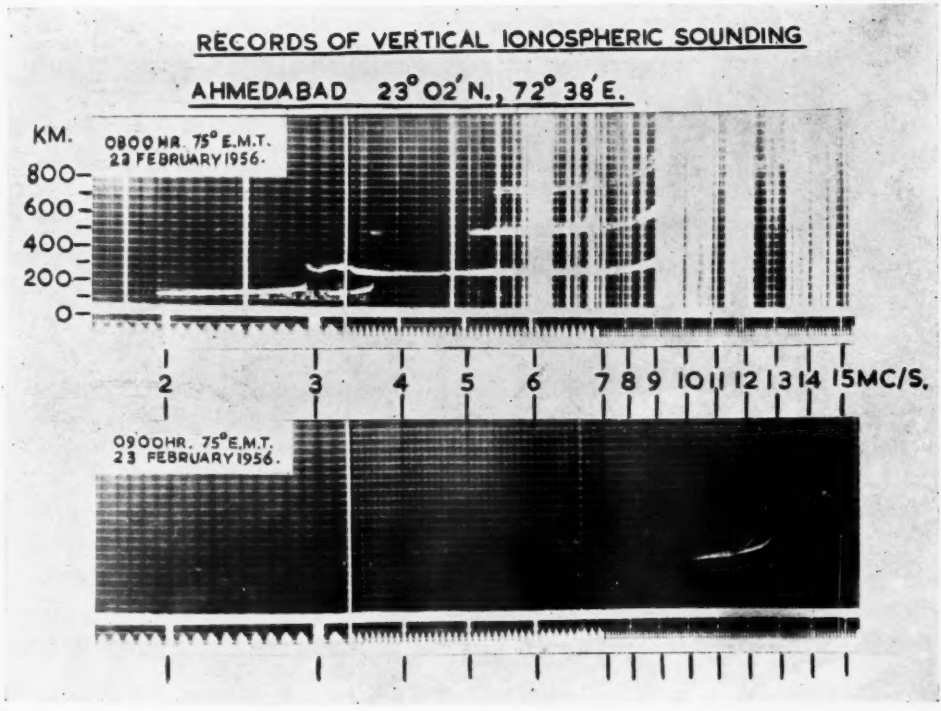

RECORDS OF VERTICAL IONOSPHERIC SOUNDING
AHMEDABAD 23° 02' N., 72° 38' E.
KM.
0800 HR. 75° E.M.T.
23 FEBRUARY 1956.
800
600
400
200
0
2
3
4
5
6
7
8
9
10
11
12
13
14
15MC/S.
0900HR. 75° E.M.T.
23 FEBRUARY 1956.

FIG. 3

A SOLAR FLARE TYPE INCREASE IN COSMIC RAYS AT LOW LATITUDES

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(*Physical Research Laboratory, Ahmedabad-9*)

Received April 27, 1956

On 23rd February 1956, the occurrence of a large solar flare was associated with a number of remarkable events observed at different stations on the earth. In addition to ionospheric disturbance, a spectacular increase of cosmic ray intensity has been reported by a number of observing stations situated in the middle latitudes.

The Physical Research Laboratory has for some years been conducting a systematic study of the ionosphere and of cosmic ray intensity at low latitudes. Continuous measurement of cosmic radio noise has been started recently. A report by Ramanathan *et al.*[1] of the events observed at Ahmedabad on 23rd February by an ionospheric recorder and a 25 Mc/s cosmic radio noise monitor is published separately. We give here the results of measurements of cosmic ray meson intensity made with standard telescopes at

1.	Ahmedabad	.. A	—73° E,	23° N,	13° N	geomagnetic, sea-level
2.	Kodaikanal	.. K	—77° E,	10° N,	1° N	„ 2,343 m.
3.	Trivandrum	.. T	—77° E,	8° N,	1° S	„ sea-level

Ahmedabad and Trivandrum are stations at sea-level.

Trivandrum and Kodaikanal are stations on the geomagnetic equator, the latter being situated at a mountain elevation. Details of the standard telescopes have been published elsewhere.[2] The telescopes measure triple coincidences of cosmic rays that can penetrate 10 cm. of lead, and which arrive in directions inclined with the vertical at an angle not exceeding 22° in the E-W plane, and 37° in the N-S plane.

I. Solar Flare Type Increase on 23rd February 1956

During the period 21–2–1956 to 25–2–1956, three independent instruments were functioning satisfactorily at Ahmedabad, while at Kodaikanal and Trivandrum there were at each station one or two independent telescopes in operation. In Fig. 1 are shown the per cent. hourly deviations of meson intensity measured by each telescope on 22nd, 23rd and 24th February. No corrections of any kind have been applied to the data. For each station hourly data from the different telescopes have been combined and the average per cent. hourly deviations are plotted. The average per cent. hourly deviations of all 7 telescopes at the three stations are also shown. In Table I we give

TABLE

Per cent. average hourly deviations of meson intensity at Ahmedabad, Kodaikanal

75° E.M.T.	21—2—1956				22—2—1956			
	A	K	T	Ave.	A	K	T	Ave.
0330 to 0030 ..	+1·58		+0·26	+0·92	−0·02	−1·17	+0·98	−0·07
0030 to 0130 ..	+0·42		−2·23	−0·91	+0·05	+0·66	+4·35	+1·68
0130 to 0230 ..	−0·02		−0·70	−0·36	+1·56	+0·83	+1·10	+1·16
0230 to 0330 ..	−0·05		−3·07	−1·56	−1·19	−0·33	+0·55	−0·32
0330 to 0430 ..	−1·86		−1·92	−1·89	+0·44	+1·50	−0·43	+0·50
0430 to 0530 ..	+0·53		−1·67	−0·57	+0·11	−1·00	−0·51	−0·46
0530 to 0630 ..	+1·01		−0·10	+0·46	+1·17	+0·34	+4·31	+1·94
0630 to 0730 ..	+0·68		−1·51	−0·42	−3·06	+0·67	+0·74	−0·55
0730 to 0830 ..	−2·36		−0·64	−1·50	−0·84	+0·34	+3·47	+0·99
0830 to 0930 ..	−2·13		+2·70	+0·29	+1·23	+1·17	+0·25	+0·88
0930 to 1030 ..	−1·09		+3·51	+1·21	+0·49	+4·33	+2·75	+2·52
1030 to 1130 ..	+0·96		−1·25	−0·15	+0·19	−0·33	+5·76	+1·87
1130 to 1230 ..	+2·38		+0·22	+1·25	−2·47	+2·34	+0·58	+0·15
1230 to 1330 ..	+0·85		−1·75	−0·45	−1·58	−0·83	+0·41	−0·66
1330 to 1430 ..	−1·12		+0·27	−0·43	+1·74	+2·67	+3·06	+2·49
1430 to 1530 ..	−2·18		−1·75	−1·97	+1·79	+3·00	−1·61	+1·06
1530 to 1630 ..	−0·60		+0·93	+0·17	−1·73	+1·00	+0·83	+0·03
1630 to 1730 ..	+0·37		−0·57	−0·10	−0·52	−3·83	−4·08	−2·81
1730 to 1830 ..	−3·17		−1·49	−2·33	−1·80	+0·50	−1·52	−0·94
1830 to 1930 ..	+1·80		−0·02	+0·89	−1·90	+2·67	−1·96	−0·39
1930 to 2030 ..	−0·95		−0·32	−0·64	+0·06	−2·35	−1·96	−1·41
2030 to 2130 ..	−1·50		−1·38	−1·44	−2·13	+1·00	−2·39	−1·50
2130 to 2230 :	−2·98		+3·08	+0·05	+2·08	−0·34	−5·16	−1·14
2230 to 2330 ..	+0·24		−2·91	−1·22	+2·40	+0·84	−2·50	+0·25

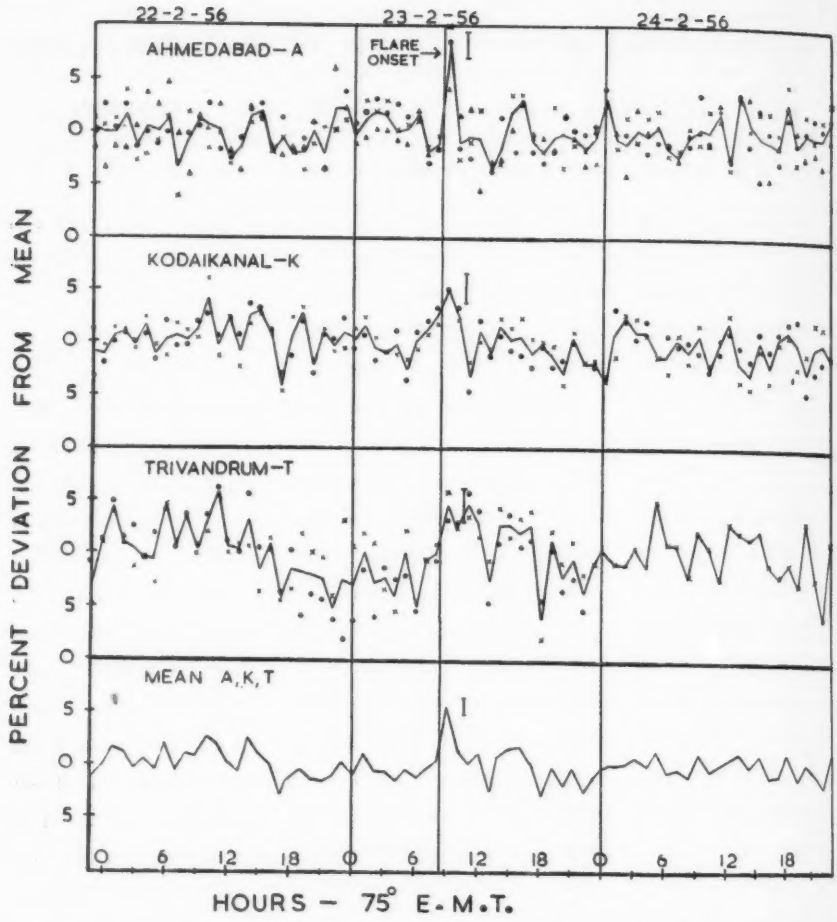
the average hourly deviations at A, K and T as well as the combined average hourly deviations for all three stations. Data commence from two days prior to the day of the solar flare and end two days following the flare. Since the

I

and Trivandrum and the per cent. average hourly deviations for the three stations

23—2—1956				24—2—1956				25—2—1956			
A	K	T	Ave.	A	K	T	Ave.	A	K	T	Ave.
−0·08	+0·33	−2·92	−0·89	+3·19	−3·45	+0·81	+0·18	+1·90	+0·83	+2·04	+1·59
+1·40	+1·50	+0·11	+1·00	−0·47	+1·00	−0·81	−0·09	−4·06	+0·83	−2·10	−1·78
+1·80	−0·67	−2·86	−0·57	−0·98	+2·33	−1·02	+0·11	+2·41	−0·66	−1·53	+0·07
+1·60	−1·00	−2·32	−0·57	+0·10	+1·33	+0·61	+0·68	−1·78	−2·00	−1·52	−1·77
0·00	−0·16	−4·15	−1·43	−0·16	+1·23	−1·22	−0·01	+3·16	+0·49	−2·40	+0·41
+0·30	−1·67	−0·02	−0·46	+0·70	−1·33	+4·89	+1·42	+1·23	+2·66	−2·13	+0·58
+1·60	+0·17	−5·10	−1·11	−1·48	−1·16	+0·81	−0·67	+0·38	+1·00	+0·06	+0·48
−1·70	+1·33	−0·75	−0·37	−2·15	+0·16	+0·81	−0·39	+0·73	−0·50	+1·18	+0·47
−1·30	+2·50	+0·06	+0·42	−0·32	−0·99	−2·24	−1·18	+0·46	+0·49	+0·69	+0·54
+7·60	+4·83	+4·57	+5·66	+0·94	+0·33	+2·24	+1·17	+0·43	+2·33	+3·62	+2·12
−0·91	+2·66	+2·60	+1·45	+0·07	−2·33	+0·61	−0·53	−0·35	−2·00	+4·76	+0·80
−0·47	−3·33	+4·61	+0·27	+2·08	−0·33	−2·44	−0·23	−1·22	+0·83	+1·97	+0·52
−0·59	+1·00	+2·89	+1·10	−2·68	+1·83	+2·85	+0·67	−0·47	−2·00	−0·17	−0·88
−3·31	−1·00	−2·60	−2·30	+3·02	−1·99	+2·24	+1·09	−0·92	−0·83	−0·66	−0·80
−1·40	+1·50	+2·60	+0·90	+0·86	−2·99	+1·43	−0·23	+1·19	+2·17	+3·91	+2·43
+1·86	+0·33	+2·66	+1·61	−0·01	+0·17	+2·24	+0·80	−1·88	+2·00	+0·98	+0·37
+2·95	+0·50	+1·86	+1·77	−0·72	−2·12	−1·02	−1·29	+1·00	+1·83	+0·25	+1·03
−0·84	−1·00	−2·61	+0·26	−1·24	+0·50	−2·24	−0·99	+3·89	+2·00	+0·74	+2·21
−1·78	−0·16	−6·26	−2·73	+2·94	+1·33	−1·02	+1·08	−0·40	+1·49	+2·36	+1·15
−0·38	−1·33	+1·24	−0·16	−1·00	+0·01	−2·85	−1·28	+1·37	−4·17	−1·46	−1·30
−0·15	−2·83	−2·13	−1·70	+0·11	−2·84	+3·05	+0·10	+0·30	+0·83	−3·15	−0·67
−0·53	−0·50	−0·54	−0·19	−0·11	−0·34	−2·44	−0·96	−0·10	−1·83	−0·73	−0·88
−1·65	−2·00	−3·56	−2·40	−0·24	−0·01	−6·11	−2·12	−0·47	−0·83	−2·31	−1·20
−0·68	−2·00	−0·81	−1·16	+1·58	−1·16	+1·99	+0·80	−0·80	+0·05	+1·55	+0·27

photographic records were made hourly at the half hours according to 75° EMT, which is almost local time at the three stations, and the onset of the flare was observed at Ahmedabad by the sudden absorption of cosmic



TEXT-FIG. 1. Per cent. hourly deviations of cosmic ray meson intensity at Ahmedabad, Kodaikanal and Trivandrum and the average of the hourly deviations at the three stations on 22nd, 23rd and 24th February 1956. The hourly deviations of each individual telescope are also indicated with appropriate symbols.

radio noise at about 0832 hours 75° EMT, we are fortunate in having the onset of the flare almost coincide with the commencement of the hourly interval over which the cosmic ray intensity is averaged.

At Ahmedabad during the hour immediately following the flare the average deviation is $+7{\cdot}6 \pm 1{\cdot}3\%$. During the same hour at Kodaikanal and at Trivandrum the average deviations are $+4{\cdot}8 \pm 1{\cdot}45\%$ and $+4{\cdot}6$

$\pm 1{\cdot}64\%$ respectively. The average hourly deviation at Ahmedabad rarely exceeds $\pm$ 3% and therefore the increase of $7{\cdot}6\%$ after the solar flare on 23-2-1956 stands out clearly. At Kodaikanal and Trivandrum the hourly deviations are much larger than at Ahmedabad and consequently the increases during the hour following the flare are not equally striking even though at both stations there are large significant positive deviations. In the average of deviations of all seven telescopes we get the advantage of suppressing deviations which are not simultaneously present at all three stations. We then have a prominent average increase of $+ 5{\cdot}7 \pm 0{\cdot}8\%$ during the hour immediately following the solar flare. This is considerably larger than other hourly deviations throughout the period. The difference between the increase at Ahmedabad and the average increase at all three stations is not significant. It is therefore not possible to comment on the difference in the flare effect due to change from 0–13° geomagnetic North latitude. There is also no significance difference between the increases at Kodaikanal and Trivandrum, in spite of the difference in elevation of about 2,343 m. But in view of the standard error of the determination at each place, the existence of a difference cannot be excluded.

II. Interpretation

The present evidence establishes for the first time the existence of a solar flare increase in cosmic rays at low latitudes near the geomagnetic equator. During the four earlier observed instances of solar flare increases in cosmic ray intensity, no significant increase was noticed at stations in latitudes less than 25°. It is difficult to say whether the present flare is unique in producing measurable effects at the Equator, since equipment comparable to ours was not operating during earlier occasions at low latitudes. As discussed later in this communication, solar cosmic rays emitted during large flares can arrive only from certain restricted directions from the sky above the instrument. This effect becomes more pronounced at low latitudes and therefore the chance of recording a significant flare type event with an ionisation chamber with omnidirectional sensitivity is rather less favourable than with a telescope pointing to an appropriate direction. It is not known so far whether the Carnegie Institution ionisation chamber at Huancayo has registered an increase after the recent flare. A negative answer will leave ambiguous the position regarding the uniqueness of the present flare since its occurrence at a time when all three stations in India were near the impact zone appropriate to positive particles originating from the sun has perhaps favoured the observation of the increases at the Indian stations as compared to Huancayo.

From evidence prior to the recent flare, the generally accepted interpretation of the solar flare increase in cosmic ray intensity was that it is caused by a burst of positively charged particles from the sun which for the purpose of this effect, appears to have a diameter of about 30° as viewed from the earth. The particles were believed to have a maximum energy of about 10 Bev and an energy distribution much steeper than the distribution of the normal primary cosmic rays. Even though increases at stations at high latitudes, such as Godhavn, Resolute and Thule have presented difficulties, since the stations lie outside normal impact zones for particles of these energies from the sun, attempts have been made to retain the postulate of solar origin by invoking the aid of interplanetary magnetic fields. The discovery of the increase at low latitudes now makes it necessary to revise some of our thinking on this subject. If the effect is caused by positively charged particles from the sun, the following conclusions would appear to result from our observation of the increase at the magnetic equator and at 13° North geomagnetic latitude where the minimum cut-off rigidity for vertical particles is about 17·0 and 16·2 Bev/Zc respectively. In order to correct for the deflection in the geomagnetic field, and to determine the energies of positive particles originating from the sun which could play a role in causing the increase of intensity, we can use the most valuable results of Brunberg and Dattner.[3]

On 23rd February 1956, the declination of the sun was − 10°. At 0900 hours local time the position of the sun, with an angular diameter of 30° as viewed from the earth, is indicated in the diagrams kindly prepared by Brunberg and Dattner for Ahmedabad and Kodaikanal and reproduced in Figs. 2 (A) and (B) respectively. It will be observed that at Ahmedabad solar protons must have energies between 35 and 65 Bev. Furthermore these particles are incident at the top of the atmosphere at directions in the N-S plane which make angles with the zenith from about 16° S–50° S. Correspondingly at Kodaikanal or Trivandrum the solar particles would have to be within an energy range 35–70 Bev and would be incident in directions from about 8° S–45° S inclined to the vertical in the N-S plane. At all three stations no particles from the sun could arrive in the E-W plane. Between the stations at the magnetic equator and at 13° N geomagnetic latitude, there is no marked change in the limits of directions of arrival of the trajectories or of the energies of allowed protons of solar origin. Moreover we have not established a significant difference between the per cent. increase of meson intensity at the three stations after the flare. It is therefore appropriate to consider the average conditions for solar protons in low latitudes in conjunction with the average increase of 5·7%.

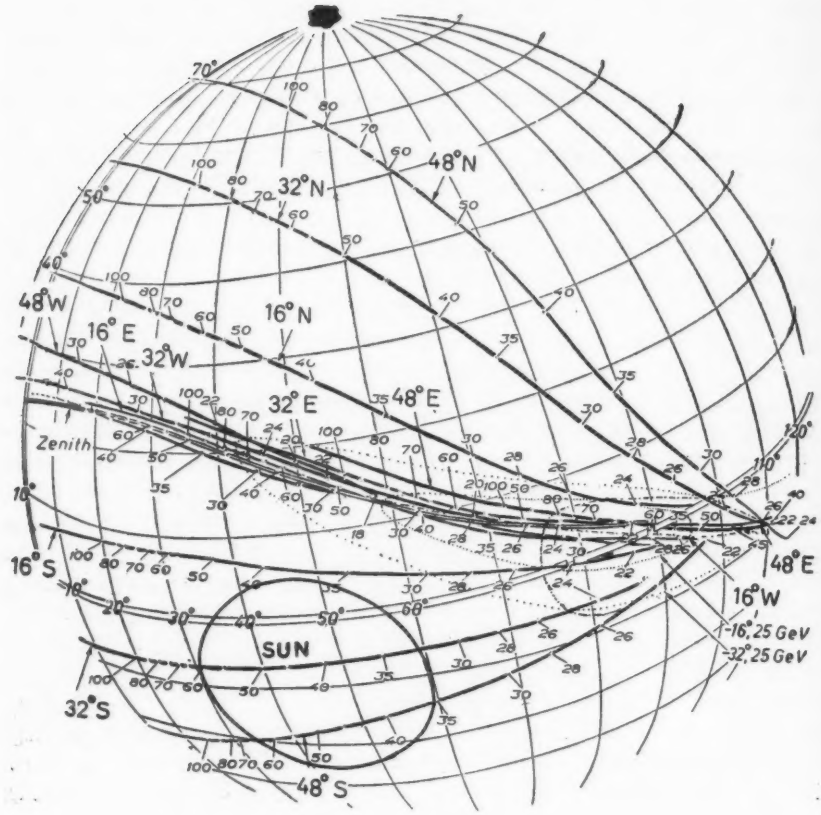
III. The Intensity of 50 Bev Solar Flare Protons

If N* be the number of primary solar protons in the energy range 35–67·5 Bev per sec. per cm.^{2} area normal to the direction of incidence, and N be the number of background cosmic rays in the same energy range per sec. per cm.^{2} per steradian, we would like to calculate the ratio $x = N^*/N$. At the present moment there are a number of uncertainties involved in relating N* and N to the corresponding counting rates n^* and n in our telescopes due to solar particles and background intensity respectively of primaries in the energy range 35–67·5 Bev. This is mainly because the published results of Brunberg and Dattner relate only to the E-W and N-S planes. We have therefore no precise way of determining the limiting directions in other azimuths which define the extent of cone which is available to the solar protons during this flare. From the interceptions of the cone on the N-S plane through zenith, and from the semi-angle of the telescopes in the same plane we estimate that solar protons can have not more than a fifth of the cone available to background intensity measured in our telescopes. Thus at the present moment we can calculate only a lower limit to the ratio x, indicative of the order of its magnitude. Under these circumstances it is appropriate to disregard a correction for the difference in the effective aperture of the telescope for solar protons and background intensity. Furthermore, since the mean primary energy for background intensity is comparable to the mean energy of 50 Bev for solar protons, we can also assume that the same multiplicity factor can be applied in each case to derive the sea-level intensity in terms of the intensity at the top of the atmosphere. Thus we have $x = N^*/N \approx 5\, n^*/n$. If n' be the counting rate due to background in the entire energy range from geomagnetic cut-off to infinity, and we assume an integral spectrum of the form $E^{-1\cdot7}$ for the primaries of background intensity, the proportionate increase of intensity

$$\cdot057 = \frac{n^*}{n'} \approx \frac{x}{5} \frac{[E^{-1\cdot7}]_{35}^{67\cdot5}}{[E^{-1\cdot7}]_{16\cdot5}^{\infty}}.$$

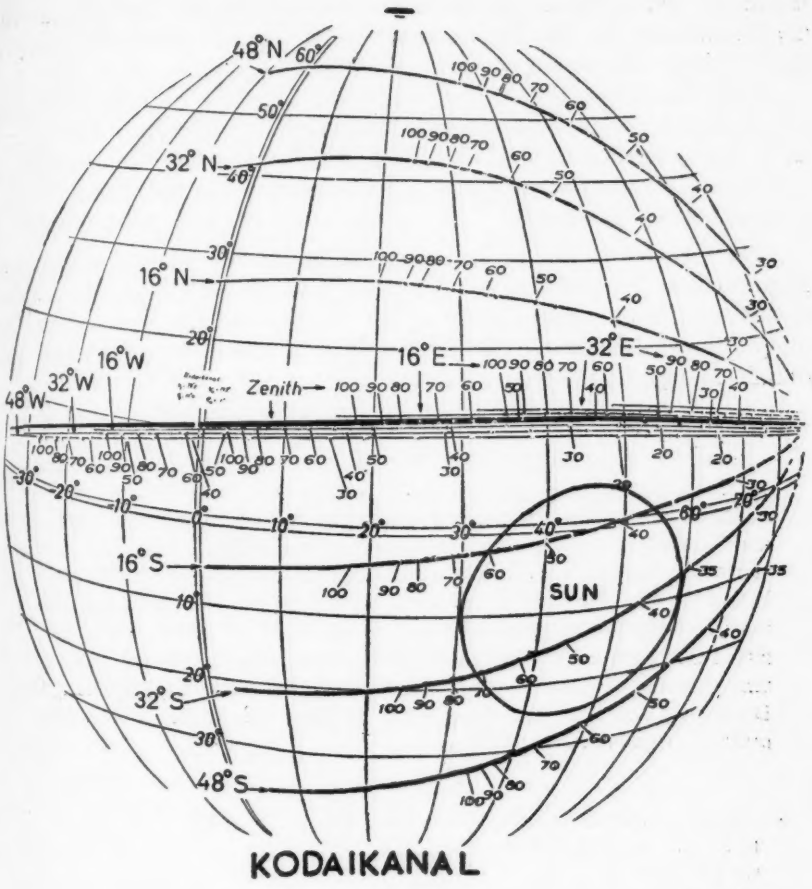
We then have $x \approx 1\cdot5$, indicating that averaged over one hour following the flare, the flux of solar protons in the energy range 35–67·5 Bev is about 1·5 times the flux of background cosmic rays in the same energy range.

Visual records indicate that the flare on 23–2–1956 was of magnitude 3 and occurred at 22·5° heliographic north and 73° heliographic west. One of the four earlier flares which produced increases of cosmic ray intensity was also located about 70° W heliographic longitude. We do not know much about the nature of magnetic fields between the sun and earth during such intense disturbances. If there is no magnetic focussing effect, we have to



TEXT-FIG. 2. Dagrams prepared by Brunberg and Dattner, showing the asymptotic co- to the zenith in the North-South and East-West Planes at (A) Ahmedabad, (B) Kodaikanal. at 0900 hours 75° EMT is marked in the diagrams. For further explanation, reference may be

accept the rather remarkable conclusion that protons of energies as great as 35–67·5 Bev can be ejected from the sun in a cone of semi-angle as large as 75°. A consequence of assuming throughout the cone a flux of solar protons as large as is observed near the earth would be that during the hour following the solar flare of magnitude 3 the sun emitted about 10^{28} protons of an energy of about 50 Bev. This may be compared with the estimate made by Simpson



B

ordinates of velocity vectors of protons of different energies incident in various directions inclined The position of the sun on 23–2–1956 with an assumed diameter of 30° as viewed from the earth, made to the original paper.[3]

et al.[4] of 2×10^{23} protons per second of mean energy 4 Bev averaged over a solar cycle due to flares of magnitude equal to or greater than 1+.

IV. Conclusion

When we consider the sharp increase of intensity and its short mean life reported by other workers who have made continuous ionisation chamber

records, we are forced to conclude that events occur on the sun which involve the acceleration of a very large number of particles to much higher energies than has been hitherto suspected or indeed thought possible. The alternative to such a conclusion might involve the abandoning of our present belief that during such events particles are actually emitted from the sun. Any modulation theory would run into the difficulty, amongst others, that the interval between the observed maximum of visual intensity of the flare and the maximum of cosmic ray intensity is only of the order of about 10–15 minutes.

We are indebted to Drs. Brunberg and Dattner for their proton-energy diagrams and to Professor H. V. Neher and Mr. Nerurkar, for helpful discussions. We are also grateful to Mr. Thakore and Mr. Vishwanath, for computational assistance. The present work is generously financed by the Atomic Energy Commission of India.

SUMMARY

During the hour following the big solar flare on 23–2–1956, an average increase of $+5{\cdot}7 \pm 0{\cdot}8\%$ has been observed in meson intensity measured with standard telescopes at Ahmedabad, Kodaikanal and Trivandrum. This is the first report of a significant solar flare type increase in cosmic rays near the geomagnetic equator. If the increase is due to solar protons travelling in approximately direct paths, the energy of the protons must extend from about 35–67·5 Bev. It is estimated that the average flux of such protons is approximately equal to 1·5 times the flux of general cosmic ray intensity in the same energy range. During the hour, the sun is estimated to have emitted more than 10^{28} protons of about 50 Bev energy.

REFERENCES

1. Ramanathan, K. R., Bhonsle, R. V., Kotadia, K. M. and Rastogi, R. G. — *Proc. Ind. Acad. Sci.*, 1956, **43**, 306.
2. Sarabhai, V., Desai, U. D. and Kane, R. P. — *Proc. Ind. Acad. Sci.*, 1953, **37 A**, 287.
3. Brunberg and Dattner .. — *Tellus*, 1953, **5**, 135; *ibid.*, 1953, **5**, 269.
4. Firor, Simpson and Treiman — *Phys. Rev.*, 1954, **95**, 1015.

HALF-LIVES OF SHORT-LIVED ACTIVITIES WITH A PULSED NEUTRON SOURCE AND A TEN CHANNEL TIME ANALYSER

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Abstract

The half-lives of He^6 and Pb^{207m} have been measured by pulsing the neutron source from a 1 Mev cascade generator and observing the decay with a ten channel cathode ray tube time analyser. A scintillation counter with anthracene crystal served as the detector. Using least squares fitting, the half-lives of He^6 and Pb^{207m} were found to be respectively $0{\cdot}852 \pm 0{\cdot}016$ second and $0{\cdot}948 \pm 0{\cdot}014$ second. Comparison with previous determinations is given.

The present paper describes a method for measuring half-lives of short-lived isotopes and isomers, from the milli-second to the second region. The half-lives of He^6 and an isomeric state Pb^{207m} have been measured with a cathode ray tube type ten channel time analyser.

The early methods for determining half-lives involved the use of mechanical devices such as a rotating wheel where the required isotope was produced at one end of the wheel by a Ra-Be neutron source and then transferred to the detector by the rotating wheel.[1] From the counting rate of the detector and the period of rotation of the wheel, the half-life was calculated.

Recent methods[2,3] employ electronic time analysers and pulsed neutron sources from low energy accelerators such as cyclotrons and cascade generators where high neutron fluxes are available. The cycle of operations is (i) A burst of neutrons is produced for a small interval to make the required isotope. The detector such as a beta-counter is not made to count the activity during this interval because of the masking of the activity by the intense neutron beam, (ii) After the neutron pulse is over, the decay of the activity produced, is counted by the detector in various time channels till the commencement of the next neutron pulse.

The pulsing of the neutron source is done by pulsing the deuteron or proton beam which produces neutrons when made to bombard a light element target. The pulsing of the beam is accomplished by pulsing the r.f. voltage

on the dees in the case of a cyclotron or by pulsing the extraction voltage of the r.f. ion source in the case of a cascade generator, as in the present case. It is also possible to pulse the deuteron or proton beam at the target end of the accelerator by electrostatic means. However, the former method is preferable because of the absence of neutron background.

The electronic time analysers built so far for such measurements were based on similar lines. For example in the work of Cassels and Latham[2] on the half-life of He^6, a ring of twelve scale circuit was driven by a master oscillator whose frequency could be adjusted. Position 1 in this ring corresponded to the pulsing of the R.F. voltage on the dees of the cyclotron and the subsequent positions 2, 3, 4, etc., connected the G.M. counter impulses through gating circuits to recording units.

Even though high neutron fluxes are obtained with accelerators, the various activities induced in the target chamber and surrounding materials by the intense neutron beam cause background problems for the detector while counting the required activity. As will be discussed later, in the present work, the background has been made smaller than the statistical fluctuations of activity counts by redesigning the target chamber and using a scintillation counter with anthracene crystal which made it possible to discriminate between the activity pulses and background.

NEUTRON SOURCE

Fast neutrons were produced from D–Be reaction using 700 Kev deuterons at 250 microamperes and a beryllium target. The neutron source was pulsed by pulsing the deuteron beam. This was done by a motor with a make and break contact arrangement for the extraction voltage of the r.f. ion source. The neutron pulse width was 200 milli-seconds and the repetition rate was one pulse for every 2·3 seconds.

EXPERIMENTAL PROCEDURE

The block diagram of the apparatus is shown in Fig. 1. The deuteron current pulse at the target was differentiated, amplified and converted into a flat pulse of constant height and duration about 50 micro-seconds to trigger the time base of the cathode ray tube type K 1159. The target pulse was differentiated to ensure that the time base started only at the end of the neutron pulse. The detector was a scintillation counter employing EMI 6262 photomultiplier with last four stages shorted and a $1{\cdot}5 \times 1{\cdot}5 \times 1$ cm. anthracene crystal. In the case of He^6 a small beryllium disc, 2 cm. diameter and 100 mg./cm.^{2} thick, was placed on the top of the crystal which therefore counted the betas from He^6 produced by fast neutron bombardment of beryllium. In the case of Pb^{207m} a block of lead $15 \times 7 \times 2{\cdot}5$ cm. was placed

between the neutron source and the scintillation counter which counted the gammas from Pb^{207m} produced by the inelastic scattering of fast neutrons from the lead block. Pulses from the photo-multiplier were amplified, shaped by diode clipping, converted into flat pulses of equal height and duration about 50 micro-seconds and were made to intensify the spot of the K 1159 tube. The spot itself was triggered by the target pulse as previously described to sweep across the ten dynodes or electron collectors at a known rate (in the

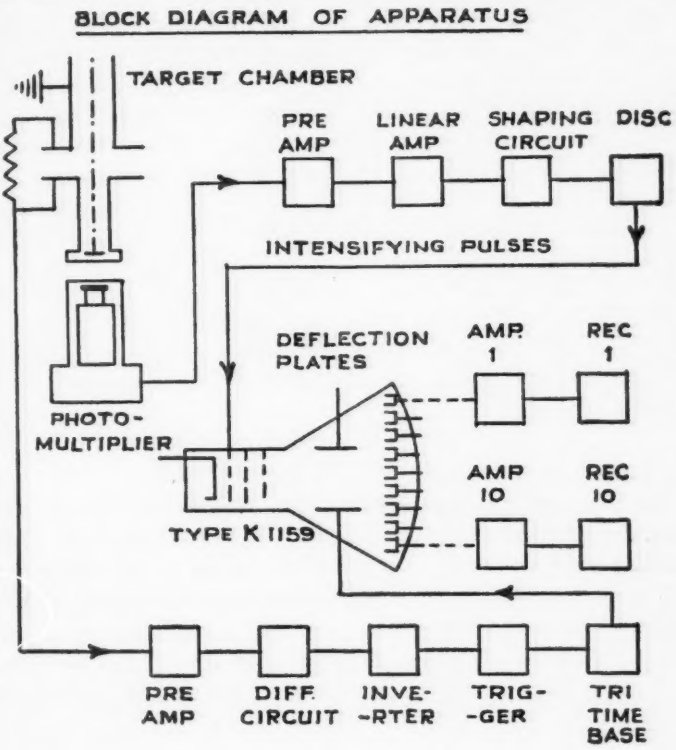

FIG. 1

present case the time taken for the spot to sweep across the ten dynodes or channels was about 1·3 seconds which was smaller than the time interval of 2·3 seconds between two neutron pulses). As the spot swept across, each photo-multiplier pulse gave a corresponding dynode pulse that was amplified by a one stage 6 AK 5 amplifier before passing on to a recording unit consisting of a scale of 32 and a high speed register. After the spot had moved past the tenth dynode it stayed stationary till it was brought back to the starting

position by the next target pulse in a time very short compared to the channel widths. The spot then swept again the various dynodes as described previously. Thus at the end of several neutron pulses the activity counts that were counted in time in the various channels due to various pulses added up in the corresponding recording circuits to give the final decay curve.

CHANNEL WIDTH MEASUREMENTS

The channel widths were measured by a chronotron whose calibration was checked by pulses from a Model 50 pulse generator with a fequency stability better than 0·5%. In order to make sure that there was no overlapping or dead space between channels, pulses from Model 50 pulse generator were made to intensify the spot of the K 1159 tube. Knowing the frequency of the pulses and the number of sweeps, the individual channel widths were calculated from the counts in various recording units of the channels. This was checked against the chronotron reading. The grid bias of the cathode ray tube was adjusted so that the chronotron method of finding the channel widths and the pulse generator method of finding the widths agreed with each other. The individual channel widths were, in general, not equal to each other due to non-uniformity in the focussing of the spot and non-uniformity in the various dynodes. The channel widths were of the order of 130 milli-seconds. The channel widths were measured before and after the experiment and the stability was found to be better than 1%.

BACKGROUND EFFECTS

In the earlier runs background counts were appreciable and this was due to the fact that the original target chamber of the cascade generator contained materials like brass, silver which became highly active due to neutron bombardment. This target chamber was replaced by a steel plate containing the beryllium target. The background effects were thus reduced and by adjusting the bias of the discriminator of the amplifier of the scintillation counter, it was possible to bring down the background counts to less than 0·5% of the observed decay rates at any particular time interval.

He^6 half-life.—A typical decay curve for He^6 is shown in Fig. 2.

The counts in each channel divided by the corresponding channel widths in second were plotted on a semi-log scale against the time corresponding to the centre of each channel. The straight line in the graph was obtained from the experimental points by the method of least squares fitting. A statistical analysis was made to make sure that the deviation of the observed points from the straight line fitted by the method of least squares is reasonable in view of

the variations inherent in the observations. From the slope of the line the half-life was calculated. Five independent determinations gave

$$\left.\begin{array}{l} 0{\cdot}864 \pm 0{\cdot}035 \\ 0{\cdot}826 \pm 0{\cdot}046 \\ 0{\cdot}847 \pm 0{\cdot}028 \\ 0{\cdot}841 \pm 0{\cdot}039 \\ 0{\cdot}874 \pm 0{\cdot}036 \end{array}\right\} \text{second}$$

The weighted mean is $0{\cdot}852 \pm 0{\cdot}016$ seocond. This value is in agreement with previous determinations.[1–7]

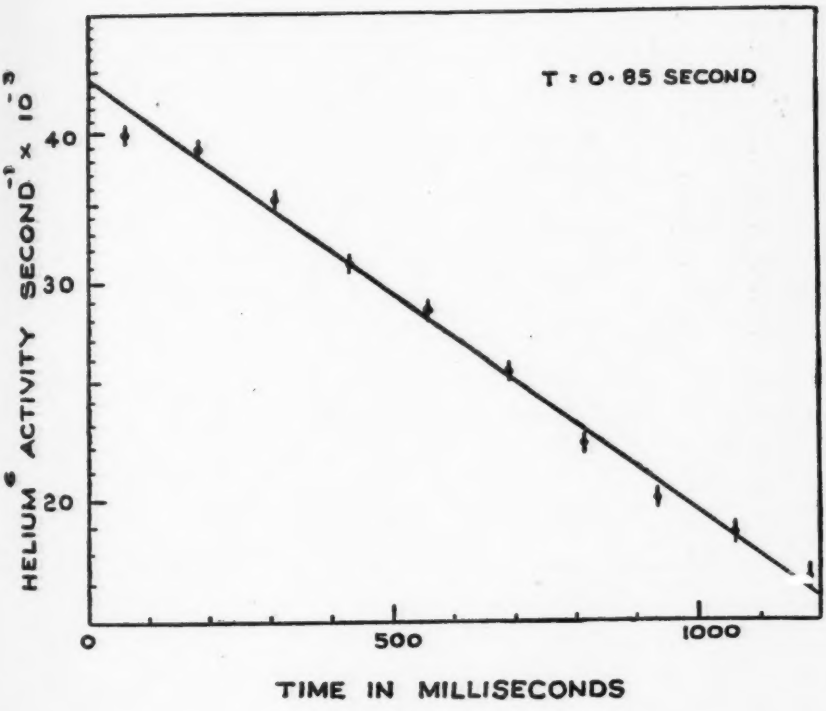

FIG. 2

Faster sweep speeds were tried and there were no other activities with lifetimes in the range from 10^{-3} to 1 second with a cross-section comparable to that of Be^{9} $(n\alpha)$ He^{6} reaction.

Pb^{207m}.—A typical decay curve for Pb^{207m} is shown in Fig. 3. Five independent determinations gave

$$\left.\begin{array}{l} 0{\cdot}933 \pm 0{\cdot}028 \\ 0{\cdot}942 \pm 0{\cdot}037 \\ 0{\cdot}962 \pm 0{\cdot}025 \\ 0{\cdot}961 \pm 0{\cdot}029 \\ 0{\cdot}919 \pm 0{\cdot}049 \end{array}\right\} \text{second}$$

The weighted mean is $0{\cdot}948 \pm 0{\cdot}014$ second.

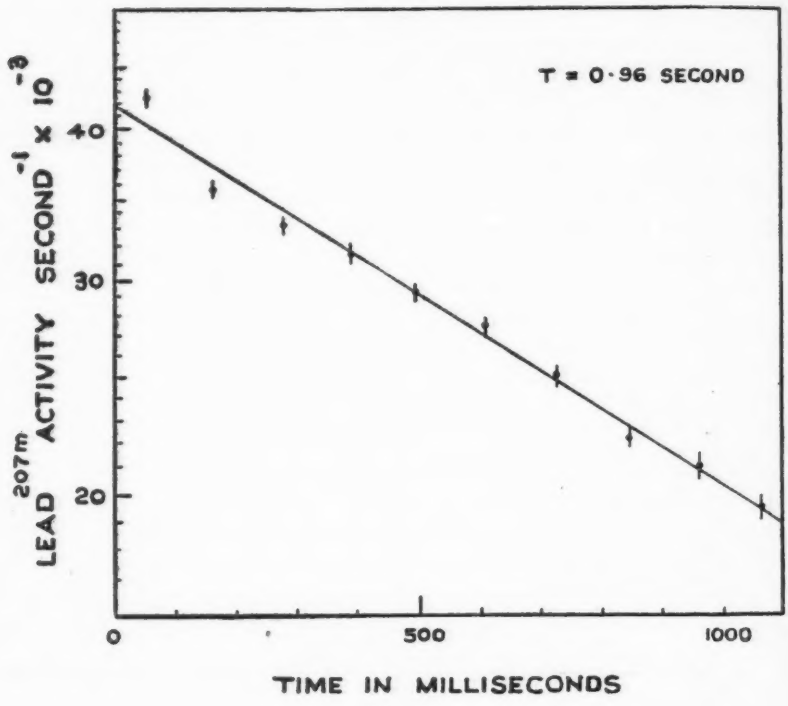

FIG. 3

This value while it agrees with that given by G. Friedlander *et al.*[11], is higher than those obtained by other workers[8–10, 12] (Table I).

In order to verify that the difference from previous determinations is not due to impurity in the lead used in the experiment, the sample was chemically analysed and the silver content was found to be only 0·003% by weight. This percentage is too small to change the half-life of Pb^{207m} by more than 0·5% since only fast neutrons were employed and the neutron pulse width was very

TABLE I

	Half-life of Pb^{207m} in second	Remarks
E. C. Campbell and Max Goodrich	0·9	Pile neutron irradiation of natural lead. Experimental details not available.
J. Lascoux and G. Vendryes	0·82±0·02	Fast neutron irradiation of natural lead. Pulsed beam and mechanical time analyser.
N. J. Hopkins ..	0·80±0·02	Experimental details not available.
G. Friedlander, Elizabeth Wilson, A. Ghiorso and I. Perlman	0·88±0·10	Lead activity separated from Bi^{207}. No details available.
J. M. Reid and K. G. Mc Neill	0·80±0·10	Lead activity produced from Pb^{208} (γ, n) Pb^{207m} and Pb^{207} (γ, γ') Pb^{207m}. Pulsed beam and electronic time analyser. No details available.

small compared to the silver half-life of 24 seconds. The other impurities have half-lives very much longer than that of silver and do not contribute to the activity. The effect of any influence of background counts on the half-life has been eliminated and it has not been possible to explain the difference from previous determinations.

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I am grateful to Dr. R. Ramanna for suggesting the problem and for his interest during the course of the work. It is a pleasure to thank Prof. D. D. Kosambi and Mr. U. V. Ram Mohan Rao, for the many helpful discussions and statistical analysis of data. My thanks are due to Dr. V. T. Athavale, for carrying out the chemical analysis. Acknowledgement is due to Messrs. P. S. Raju and C. S. Somanathan, for help in taking readings and the wiring of the associated electronic equipments and Mr. S. K. Amberdekar, for running the accelerator.

REFERENCES

1. Holmes, J. E. R. .. *Proc. Phys. Soc.*, 1949, **62 A**, 293.
2. Cassels, J. M. and Latham, R. *Nature*, 1947, **159**, 367.
3. Battat, M. E. and Ribe, F. L. *Phys. Rev.*, 1953, **89**, 80.

4. Sommers, H. S. and Sherr, R. — *Phys. Rev.*, 1946, **69**, 21.
5. Allen, K. W., Burcham, W. E. and Wilkinson, D. H. — *Proc. Roy. Soc.*, 1947, **192 A**, 114.
6. Knox, W. J. .. — *Phys. Rev.*, 1948, **74 B**, 1192.
7. Vendryes, G. .. — *Compt. rend.*, 1951, **233**, 858.
8. Campbell, E. C. and Max Goodrich — *Phys. Rev.*, 1950, **78**, 640.
9. Lascoux, J. and Vendryes, G. — *Compt. rend.*, 1951, **233**, 858.
10. Hopkins, N. J. .. — *Phys. Rev.*, 1952, **88**, 680.
11. Friedlander, G., Elizabeth Wilson, Ghiorso, A. and Perlman, I. — *Ibid.*, 1953, **91**, 498 A.
12. Reid, J. M. and McNeill, K. G. — *Proc. Phys. Soc.*, 1953, **66 A**, 1179.

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ERRATA

On page 250, No. 4 of this Volume, Equation (8) should read as follows:—

$$(v_1^2 - v_2^2)^2 = (v'^2 - v''^2)^2 + (2\Gamma_2)^2$$

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CONTENTS

PAGE

Conveyor Belt Method for Studying Short-Lived Activities: Ag^{108}, Ag^{110} and In^{116} . . . . . M. C. Joshi and B. V. Thosar 255

Studies on Hexachloroceric Acid. III. Reaction between Hydrated Ceric Oxide and Hydrogen Chloride Gas in the Absence of Solvents . . . . . S. S. Moosath and M. R. A. Rao 265

Studies on Hexachloroceric Acid. IV. Thermal Decomposition of Hexachloroceric Acid . . . . . S. S. Moosath 272

Spectrophotometric Estimation of Uranium (VI) by Morellin . . . . . B. R. Lakshman Rao and C. C. Patel 276

Studies on the Kinetics of the Decomposition of Murexide in Acid Solutions . . . . . N. A. Ramaiah, S. L. Gupta and Vishnu 286

Polarographic Studies of Murexide—I . . . N. A. Ramaiah and Vishnu 297

The Great Solar Flare of February 23, 1956 and Associated Ionospheric Effects at Ahmedabad . . . . . K. R. Ramanathan, R. V. Bhonsle, K. M. Kotadia and R. G. Rastogi 306

A Solar Flare Type Increase in Cosmic Rays at Low Latitudes . . . . . V. Sarabhai, S. P. Duggal, H. Razdan and T. S. G. Sastry 309

Half-Lives of Short-Lived Activities with a Pulsed Neutron Source and a Ten Channel Time Analyser . . . . . N. Veeraraghavan 319